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DETAILED STUDY OF THE INFLUENCE OF EXPERIMENTAL CONDITIONS ON RETENTION TIME IN SIZE-EXCLUSION CHROMATOGRAPHY OF BITUMENS / HEAVY OILS / ASPHALTENES

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Final Report

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(DSS File No. 03SQ.23440-5-9134-1)

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EXECUTIVE SUMMARY

This final report presents and discusses the results of CANMET research contract on the "Detailed Study of the Influence of Experimental Conditions on Retention Time in Size-Exclusion Chromatography of Bitumens/Heavy Oils/Asphaltenes" (DSS File No. 03SQ.23440-5-9134-1). The work was conducted jointly by Guelph Chemical Laboratories (GCL) and the Ontario Research Foundation (ORF).

The work program included an initial literature review of studies on the effect of secondary interactions on retention time and attempts to minimize such interactions in size-exclusion chromatography (SEC) of heavy crudes, e.g. bitumens, heavy oils and asphaltenes. Based on the literature search, two SEC packings - polystyrene gel and silanized porous silica and four solvent systems, namely o-oxylene, 1,2,4-trichlorobenzene (TCB), pyridine and tetrahydrofuran (THF) were selected for their potential success in reducing secondary interactions, and a series of SEC

experiments with model compounds using the selected packings and solvents at various temperatures were then performed to study the variations of retention time as a function of experimental conditions. Model compounds studied are standards representative of various classes of compounds present in heavy crudes, e.g., saturates, polynuclear aromatics (PNA), N- and O-PNA, and polystyrene (to simulate asphaltenes).

Initially, SEC conditions of column packings, solvent and temperature were optimized by model compound studies and column calibrated by plotting log MW vs retention time. The method was then used for the molecular weight (MW) and molecular weight distribution (MWD) analysis of five heavy crude samples (provided by Energy Research Laboratories) using the best calibration fit. Additional studies included determination of number average molecular weight (Mn) of the five samples by vapour pressure osmometry (vpo) and freezing point depression (fpd) methods. The samples were also analysed for intrinsic viscosity. The results of the above studies are described in this report.

Model compound studies on polystyrene gel packings (Waters 1000 Å +500 Å +500 Å Ultrastyragel columns in series) in o-xylene, THF and TCB have shown that the polystyrenes (PS) and saturates elute in the expected order with the largest molecules eluting first, i.e. the retention time is related to the MW. Calibrations for both types of compounds are linear in the three solvents - in TCB

they fall in one line, but in o-xylene and in THF with different slopes. In all three solvents, the PNA compounds including the N- and O-PNAs exhibit anomalous elution pattern indicating strong adsorption/partitioning on the polystyrene gels. Temperature is found to have no significant effect on the retention time. It is concluded that the gels are not appropriate SEC packings for determining molecular weight distribution of heavy crudes because of lack of corelation of retention data onto a single calibration line.

Studies with deactivated silanized silica packings (Dupont Zorbax PSM 60-S - 2 columns in series) have shown that adsorption/partitioning secondary effects of various classes of mode) compounds can be minimized or prevented in o-xylene and THF (but not in TCB and pyridine). In such systems, MW/retention time data for all but a few compounds, e.g. acridines, O- PNA correlate fairly well onto a single calibration line. Those two systems were therefore used for determining molecular weight distribution of the heavy crude samples.

The accuracy of the SEC molecular weight method is compared with vpo and fpd Mn values of the heavy crude samples and the limitations of the method discussed. Studies using suitable model compounds, and longer deactivated silanized silica columns with different pore size are required to determine the accuracy of the SEC system for molecular weight distribution of heavy crudes.

RAPPORT FINAL

ETUDE DETAILLE DE L'INFLUENCE DES CONDITIONS EXPERIMENTALES SUR LE TEMPS DE RETENTION EN CHROMATOGRAPHIE PAR FILTRATION SUR GEL DES BITUMENS/HUILES LOURDS/ASPHALTENES.

SOMMARIE

Ce rapport final présent les résultats du contrat de recherche de CANMET sur "l'Etude Détaillée de l'Influence des Conditions Expérimentales sur le Temps de Rétention en Chromatographie par Filtration sur Gel des Bitumens / Huiles Lourds / Asphaltenes" (archive DSS No. 03SQ 23440-5-9134-L). Ce travail a été réalisé par "Guelph Chemical Laboratories (GCL)" et "l'Ontario Research Foundation (ORF)".

Le plan de travail comprends une revue bibliographique des études sur l'éffet des interactions secondaires sur le temps de rétention et des tentatives réalisées afin de minimiser ces interactions en chromatographie par Filtration sur Gel (CFG) des coupes lourdes telles que les bitumens, les huiles lourds et les asphaltenes. En se fondant sur les donnés bibliographiques, deux garnissages CFG -du gel de polystyrène et de la silice poreuse silanisée- et quatre solvants -o-xylène, benzène, 1,2,4-trichloro-benzene (TCB), pyridine et tétrahydrofuranne (THF)- ont été choisis, étant donné leur capacité potencielle de réduire les interactions secondaires, et par la suite, une série d'expe-

riences ont été réalisées afin de déterminer les variations du temps de rétention en fonction des conditions experimentales, en employant pour ceci des composés modèles et les garnissages et solvants indiqués plus haut a plusieurs températures. Les composés modèles étudiés sont des standards représentatifs de plusieurs types de composés présents dans les coupes lourdes, comme par example des saturées, des aromatics polynuclaires (PNA), N- et 0-PNA, et d polystyrène (afin de simuler les asphaltenes).

Dans un premier temps, les conditions CFG du garnissage des colonnes, les solvants et la température ont été mis au point par des études, avec les composés modèles et les colonnes ont été etalonnées en portant log PM en fonction du temps de rétention. La méthode a été ensuite employée pour la détermination des poids moléculaires (PM) et des distributions de poids moléculaires (DPM) de cinq échantillons des coupes lourdes (Fournis par "Energy Research Laboratories") en utilisant pour ceci la meilleur courbe d'étalonnage. Des études additionnales ont compris par ailleurs, la détermination de l'indice moyen de la distribution des poids moléculaires des cinq échantillons par les méthodes d'osmométrie de pression de vapeur (OPV) et de dépression du point de congélation (DPC). La viscosité intrinsèque des échantillons a été également analysée. Les

résultats de cettes études sont décrits dans ce rapport.

Les études réalisées avec les composés modèles et le garnissage du gel de polystyrène (des colonnes Waters 1000 A + 500 A + 500 A + Ultrastyragel en série) dans du o-xylène THF et TCB ont montrée que les polystyrènes (PS) et saturées sont élués dans l'ordre attendu avec les plus grandes molécules en premier, ce qui indique l'existence d'une correlation entre le temps de rétention et le PM. Les correlation pour les deux types de composés sont lineares dans le trois solvants - dans du TCB la pente est la même pour les deux tandis que dans de l'o-xylène et du THF les pentes son differents. Dans les trois solvants, les composés PNA comprennant les N-et les O-PNA présentent un profile d'élution anormal ce qui est indicatif d'une forte adsoption/partage, dans les gels de polystyrène. Il a été trouvé que la température n'a pas d'éffet significatif dans le temps de rétention. Il a été conclu que les gels ne sont pas de garnissages appropriés pour la détermination de la distribution des poids moléculaires des coupes lourdes étant donné la manque de corrélation des donnés de rétention dans une simple droite d'étalonnage.

Les études avec les garnissades de silice silanisée desactivée (colonnes, Dupont Zorbax PSM 60-S-2 en série) ont montrés que les éffets secondaires sur la

adsorption/partage des plusieurs types des composés modèles peuvent être minimisés ou prévenus dans du o-xylène et THF (mais pas dans du TCB et de la pyridine). Dans ces systèmes, il y a une bonne correlation lineare entre les PMs et les temps de rétention pour tous les composés, avec quelques exceptions telles que les acridines et les N-PNA. Par consequent ces deux systemes ont été utilisés pour la détermination de la distribution des poids moléculaires des échantillons des coupes lourdes.

Le precision de la méthode CFG pour la détermination des poids moléculaires a été comparée avec les valeurs OPV et DPC pour les échantillons, des coupes lourdes, et les limitations de la méthode ont été discutées. Des études employant des composés modèles appropriés, et des colonnes de silice silanisée desactivée, plus longues avec plusieurs tailles de pore sont necessaires afin de déterminer la précision des systèmes CFG pour la détermination de la distribution des poids moléculaires des coupes lourdes.

Final Report

DETAILED STUDY OF THE INFLUENCE OF EXPERIMENTAL CONDITIONS ON RETENTION TIME IN SIZE-EXCLUSION CHROMATOGRAPHY OF BITUMENS/HEAVY OILS/ASPHALTENES

1. INTRODUCTION

This report for the CANMET/ERL contract research program on the development of new SEC (Size-Exclusion Chromatography) concepts is submitted by Guelph Chemical Laboratories (GCL), Guelph, Ontario. The work was conducted jointly by GCL and Ontario Research Foundation (ORF), with ORF acting as subcontractor for GCL.

Vapour pressure osmometric and cryoscopic molecular weight determination and viscosity measurement of the heavy crude samples were performed by GCL, and studies on the other aspects of the project were carried out at ORF.

1.1 Background

The determination of molecular weight is an important tool in the characterization of heavy oils, bitumens, asphaltenes and their synthetic crude products. Several methods are used to measure the average molecular weight of this type of sample, but size-exclusion chromatography (SEC) has the advantage of providing the molecular weight distribution at the same time. However, it has been demonstrated that the molecular weight determination of heavy oils and related materials by SEC can be erroneous due to the variety of compound classes present in such samples which exhibit unusual retention characteristics. Size-exclusion chromatography is widely used for the

analysis of polymers. Since polymers are composed of thousands of identical units, SEC is a true representation of the molecular weight distribution because interactions between solute and packing or solvent are identical for molecules of all sizes. In heavy oils, bitumens and other similar samples, several types of molecules are present and it is expected that interaction between these molecules and the packing or the solvent will be different. Studies to prevent or minimize such secondary interactions are, therefore, necessary in order to use the SEC method for the determination of molecular weight and molecular weight distribution of bitumen/heavy oils.

1.2 Objective

The purpose of this contract is to study experimental conditions that would minimize secondary interactions which lead to retention time variations in size-exclusion chromatography. Ideally, retention time differences for compounds having the same molecular weight should be restricted to hydrodynamic volumes, independently of the type of molecules.

For that purpose, a series of experiments using different solvents and conducted at various temperatures shall be performed to see the variations of retention time as a function of experimental conditions.

The work plan under this contract program of developing new SEC concepts included the following:

1) Perform an initial literature review of studies on the effect of secondary interactions on retention time and attempts to minimize such interactions in SEC of bitumens, heavy oils and asphaltenes (heavy crudes).

2) Based on the literature search, select two appropriate packings and three solvents or solvent systems for their potential success in reducing the secondary interactions and perform a series of SEC experiments with heavy

crude simulating model compounds using the selected packings and solvents at various temperatures to study the variations of retention time as a function of experimental conditions. Model compounds to be studied are standards representative of various classes of compounds present in heavy crudes [saturates, aromatics, condensed polynuclear aromatics (PNA), N- and O-PNA. High molecular weight polymers, e.g. polystyrenes are also included to simulate asphaltenes].

3) Perform SEC analysis of five selected heavy crude samples for molecular weight (MW) and molecular weight distribution (MWD) using calibration curves of standards prepared under best SEC conditions as determined in Task 2.

4) Analyze the five selected heavy crude samples by other molecular weight measurement techniques such as vapour pressure osmometry (VPO), cryoscopy/freezing point depression (FPD) and/or light scattering.

5) Determine viscosity of the high molecular weight polystyrene model compounds and the five heavy crude samples in order to relate to their hydrodynamic volumes.

1.3 Literature Search and Selection of SEC Conditions

The initial phase of the program involved a comprehensive literature search of studies on the effect of secondary interactions and influence of molecular shape on retention time and attempts to minimize such interactions in SEC. The sources of information used for the search were relevant books, publications received at ORF and communications with other researchers familiar with SEC studies of heavy crudes and coal liquids. Another source was the ORF library computerized literature search using the data access system that includes CAN/OLE, ELHILL, ORBIT and DIALOG, and data bases that include CAC, SCISEARCH, NTIS, DOE, EMERAY LINE and ENERGY NET. Relevant literature reviewed is cited in the References (Section 4) of the report.

1.3.1 Effect of Secondary Interactions and Molecular Shape on Retention Time

Size-exclusion chromatography separates molecules by molecular weight/molecular size and not by chemical structure. However, a number of workers have reported that factors other than mere molecular weight/size have an influence on the emergence of solutes during SEC on cross-linked polystyrene gels[1-6]. For instance, Hendrickson & Moore[1] have suggested that the following four basic factors might be expected to modify the retention time of compounds in SEC:

1) adsorption of solutes onto or into the gel surface

2) solvent-solute association, e.g. hydrogen bonding of-OH compounds with ethers such as THF

3) solute-solute interactions, e.g. dimerization of solute molecules such as acids, and

4) intramolecular bonding.

Studies on elution behaviour of about 100 intermediate and low molecular weight model compounds selected from compound classes of n-alkanes and cycloalkanes, alcohols, aromatics, carboxylic acids, amines and others on polystyrene gels with THF as eluting solvent have been reported by Edwards and Ng[2]. They have observed that the properties of compounds other than molecular weight/size appear to have the greatest effect on elution characteristics of solutes, and concluded that such anomalous behaviour in SEC is the result of solute molecules associating with solvent, the gel packing or themselves. Some specific observations relevant to our study are as follows:

1) In comparison with the elution behaviour of n-alkanes, a decrease in retention time (i.e., an increase in effective molecular size) is observed with alcohols, carboxylic acids, aromatics and compounds with active hydrogen species due to hydrogen bonding of the solute with the ether group in THF;

2) Aromatics are held in the column longer than alkanes resulting in smaller molecular sizes. This is due to association between the aromatic solute and the gel packing since both are aromatic.

Cazes and Gaskill[6] studied the effect of solute-solvent association in SEC separation of a number of polar and non-polar low molecular weight compounds on polystyrene gels using THF as well as o-dichlorobenzene as the eluting solvents. They have observed the polar compounds to emerge early in THF (a strongly basic associating solvent) indicating solute-solvent interactions. According to them, these interactions can be prevented if the SEC is performed in a non-associating solvent like o-dichlorobenzene. They have shown that all data points (elution volume vs molar volume) of n-saturated hydrocarbons, alcohols and a number of other compounds (aromatics, acids) possessing permanent dipoles of varying magnitude fall on or near a single line.

The characterization of heavy crudes (bitumen, heavy oil and asphaltene) for molecular weight and molecular weight distribution by SEC has generally been a problem due to non-ideal elution behaviour of components present in heavy crudes, particularly the low molecular weight constituents. Studies have indicated that SEC separations of heavy crude components occur, not as a function of a single parameter but as a complex function of molecular size, shape and polarity. A heavy crude sample contains components of widely differing polarity, e.g. non-polar paraffins and naphthenes, moderately polar aromatics [mononuclear aromatics, Cata-* (less condensed) and Peri-condensed** (highly condensed) PNA], polar N- and O- containing PNA heterocyclics and highly polar constituents with phenolic and carboxylic acid functionalities.

* Cata-condensed PNA - four carbons added to two already in the system to form a new ring, e.g. naphthalene, anthracene, phenanthrene

** Peri-condensed PNA - three carbons added to three already in the system to form new rings, e.g. pyrene, perylene, coronene.

Each class of these compounds will interact with the SEC packings and the solvent, and will interact with each other to a different degree depending upon the packing, solvent and temperature used in SEC. The strength of the interaction increases with increasing solute polarity and decreasing solvent polarity. As a result, the determination of molecular weight (MW) and molecular weight distribution (MWD) of bitumen/heavy oil/asphaltenes can be erroneous, since the retention times of certain components (solutes) may be shifted to either a) higher retention times (and therefore to smaller molecular sizes) due to solute-packing interactions, in which case the fundamental size-exclusion process is complicated by superposition of an adsorption phenomenon, or b) to shorter retention times (and therefore to larger molecular sizes) due to solute-solvent/solute-solute interactions, in which case the fundamental size-exclusion process is complicated by superposition of an association phenomenon.

Heavy crude model compound studies[7-10] in tetrahydrofuran (THF) and methylene chloride (CH_2Cl_2) using polystyrene-divinylbenzene gel packing have shown that the plot of log molecular weight or molar volume (hydrodynamic volume) against retention time gives different relations for the following groups of model compounds representative of the types present in bitumen/heavy oil/asphaltenes: 1) n-alkanes, 2) mononuclear aromatics, 3) less condensed (Cata) PNA aromatics, 4) highly condensed (Peri) PNA aromatics, and 5)N-heterocyclics. Typical calibration curves in THF and CH_2Cl_2 with polystyrene gels shown in Figure 1 have indicated the following:

a) n-alkanes yield linear curve with decreasing molar volume for increasing retention time as is expected in SEC. The mononuclear aromatics, e.g. benzene falls in line on the n-alkanes curve.

b) The less-condensed (Cata) PNA compounds also follow a linear curve with decreasing molar volume for increasing retention time, but with considerably steeper slope than the curves for the n-alkanes/monoaromatics.

c) Anomalous behaviour is shown by the highly-condensed PNA compounds. They show an increase in molar volume with increasing retention time, suggesting a predominant adsorption or partitioning rather than a size-exclusion effect.

d) The N-heterocyclics follow the same elution pattern as the highly-condensed PNA compounds.

The above anomalous retention characteristics of highly-condensed PNA and heterocyclics are thought to be due to the interaction of their pi (π) system with the highly aromatic polystyrene gel packings. This interaction is probably enhanced by their poor solubility in the THF, CH_2Cl_2 mobile phases. Reported SEC work[8] on asphaltene in THF/polystyrene gel system has shown the presence of tailing in the chromatogram indicating delayed elution due to adsorption from similar solute-gel interaction.

In addition to the above solute-gel interactions, errors in MW characterization may also be caused by molecular association due to solute-solvent or solute-solute interactions. Such associations result in an increase in molecular size and, therefore, cause certain polar molecules to elute at lower retention times than is expected in SEC. For example, when THF which is known to form hydrogen bonded complexes with a number of compounds and to interact with Athabasca bitumen[11] is used as the solvent, certain species containing phenolic OH, carboxylic acid, amine, amide and other polar functionalities present in heavy crudes/asphaltenes can form hydrogen bonds with the ether group in THF or undergo dipole-dipole interactions with THF, effectively producing a molecule which exhibits a greater linear molecular size and a smaller retention time. A similar elution pattern by the erroneously high molecular size can also be anticipated from solute-solute association in a solvent of low dielectric constant, e.g. benzene. For instance, carboxylic acid is known to undergo dimerization, and asphaltenes can form micellar associations in benzene. However, this type of association can usually be eliminated by using a more dilute solution or a solvent of higher dielectric strength.

Ideally, in the absence of any secondary interactions, similar molecular weight compounds are expected to show identical retention times, provided the compounds do not differ in molecular size and shape. However, in a solute mixture containing a variety of chemical types, the molecular size and shape (expressed as molar volume or hydrodynamic volume) may not be identical for all components of equal molecular weight. This is especially true for heavy crude types of samples. These samples are not homologous mixtures differing only in molecular weight. They are mixtures of components having different configurations, ranging from largely paraffinic worm-like molecules to compact, nearly spherical or disk-shaped polynuclear aromatic ring system. Therefore, even in ideal cases, there will be SEC retention time differences for heavy crude components having the same molecular weight but differing in molecular size and shape.

Influence of molecular shape on SEC retention behaviour of more than a hundred polynuclear aromatic hydrocarbon materials has been studied by Edstrom and Petro[12] in THF/polystyrene gels @ 25°C. The model compounds studied included various monoaromatics, diaromatics and polynuclear aromatics (3-ring and greater) and their alkyl, naphthyl and phenyl substituted derivatives, N-PNA, hydrogenated and oxygenated PNA. They have observed that substitutes can alter elution behaviour considerably, depending on position on the aromatic nucleus, e.g. 9-methyl anthracene elutes at 191.5 mL whereas 2-methyl anthracene elutes at 185 mL, yet they are similar molecular weight compounds. Similar observations were made with three dimethylnaphthalene isomers. For example, 1,5 isomer eluted at 192.0 mL, whereas 1,2- and 2,3-dimethylnaphthalene eluted at 190.5 and 187.0 mL, respectively. They attributed the above retention time differences to the effect of methyl substituents at different positions on the normal planar configuration of the aromatic ring structure. They also observed that the hydrogenation of the aromatic ring can distort the rings from their normal planar configuration and introduce a three dimensional effect. Five membered rings and the rings containing hetero N and O atoms also introduce distortion in the planarity of many multi-ring molecules. The introduction of oxygen and nitrogen on the molecule has the additional effect of polarization which can further complicate the elution behaviour by association effects.

1.3.2 Attempts to Minimize SEC Secondary Interactions

Very little information is available in the literature on studies aimed at minimizing secondary interactions in heavy crude SEC work. All work to date has been performed with cross-linked polystyrene gels as the column packing. THF, CH_2Cl_2 and chloroform are widely used as eluting solvents for many SEC separations because of their low refractive index and viscosity, and the good swelling abilities of the packing. Also, they dissolve a wide range of polymers, and are good solvents for heavy crudes including asphaltenes and coal liquids. However, as stated earlier, the highly condensed PNA and N-heterocyclic PNA model compounds show non-ideal retention behaviour in such solvents.[7,8,12] Other solvents such as THF + 10% methanol, chloroform + 5% methanol, toluene, benzene and benzene + 5% methanol have been used,[8,14] but satisfactory suppression of adsorption has not been achieved. The only reference cited in the literature for suppressing the adsorption of highly condensed PNA on polystyrene gels is the reported SEC work by Bergman et al.[8] They have reported that the anomalous elution behaviour of condensed PNA (but not the N-PNA) disappears when 1,2,4-trichlorobenzene (TCB) is used as the SEC solvent. (See calibration curve in TCB in Figure 1). The authors performed most runs at 140°C, but they found that TCB can overcome the anomalies even at room temperature. The authors also studied the elution behaviour of numerous model compounds including n-alkanes, Cata- and Peri-condensed PNA and N-PNA heterocyclics, and found an increasing elution anomaly with decreasing sample solubility in different solvents. This may indicate that partitioning rather than adsorption causes non-ideal SEC retention behaviour.

1.3.3 Selection of SEC Conditions

The foregoing literature review has indicated the following:

1) Adsorption onto or into gel surface and partitioning due to solubility difference are important in SEC of polynuclear ring systems including N- and O- heterocyclic aromatics.

2) The non-ideal elution behaviour of PNA and heterocyclic PNA generally result in a non-linear calibration curve at low molecular weights for heavy crude samples.

3) Development of new SEC concepts is necessary in order to minimize or prevent the above interactions so that SEC fundamental size-exclusion process predominates.

4) In order to be truly representative of the majority of the PNA compounds present in heavy crudes, studies on elution behaviour of alkyl substituted PNA class of model compound are necessary, since they represent majority of the PNA compounds present in heavy crude. The alkyl substitution on the PNA ring system will minimize the adsorption because such substitution is known to increase solubility as well as to prevent (by shielding the aromatic ring) the interaction of the π system with the aromatic polystyrene gels.

5) The claim that purely size separation can be accomplished by the use of TCB as eluting solvent should be tested. An alkyl substituted aromatic solvent such as xylene, α-methyl naphthalene should also be tested as SEC solvent because of good solvent power.

6) Alternative supports should also be tried, for example, deactivated silica or porous glass. Any interaction between the solute and the support (the so-called solute-gel interaction) would probably then be prevented.

7) The effect of temperatures should be studied since solute interactions with the packing surface at higher temperature will be minimized due to the enhanced solubility of the solutes in the mobile phase.

For the present study, we selected four solvents, 1) o-xylene, 2) TCB, 3) pyridine and 4) THF, in order to evaluate their potential in reducing secondary interactions on two packings - polystyrene gels and the silanized porous silica. A series of experiments using the selected packings and solvents were then carried out at various temperatures to study the variations of retention time as a function of experimental conditions.

Initially, SEC conditions of column packings, solvent and temperature were optimized by analysis of a number of model compounds representing various classes of compounds present in heavy crudes, e.g. saturates, PNA (3-ring or less), PNA (> 3-ring), N- and O-PNA. Polystyrenes were included in the list of model compounds to simulate high molecular weight asphaltenes. The method was then used for the MW and MWD analysis of five selected heavy crude samples using the best calibration fit. Additional studies included determination of number average molecular weight of the five samples by two alternative methods - cryoscopy and vapour pressure osmometry. The samples were also analyzed for intrinsic viscosity. The results of the above studies are described in this report.

2. EXPERIMENTAL

2.1 Details of Facilities

2.1.1 SEC Retention Time Experiments

SEC System:

For the retention time experiments with model compounds, an SEC system consisting of the following components was used:

1) Waters Model HPLC Pump

2) Waters Model Autosampler

3) Waters Model 410 Differential Refractive Index (RI) detector with advanced thermal control (30°C - 50°C) and optics.

4) Waters Programmable Column Temperature Control System (TCM): upper temperature limit - 150°C

5) Waters Model Data Module for acquisition of retention time data

For calibration plots (log MW vs retention time and log molar volume vs retention time), an Apple computer Macintosh with MacDraw graphic package was used.

Columns

Columns used for the SEC work were of the following types:

1) Polystyrene Gels: For initial screening work, three (3) prepacked Waters Ultra-Styragel columns of 10^3Å + 100Å + 100Å pore sizes in series (10 μm particle size; each column 7.8 mm i.d. x 30 cm long; MW range: 100-30,000) were used. For final experiments, three (3) prepacked Waters Ultra-Styragel columns of 10^3Å + 500Å + 500Å pore sizes in series (10 μm particle size; each column 7.8 mm i.d. x 30 cm long; MW range: 100-30,000) were used.

2) Silanized Silica Porous Packings: Two (2) prepacked DuPont's Zorbax PSM 60S columns of 60Å + 60Å pore sizes in series (6 μm particle size; each column 6.2 mm i.d. x 25 cm long; MW range: 100-20,000) were used.

The SEC column set was equipped with a precolumn filter (Waters Associates).

2.1.2 Analysis of Heavy Oil/Asphaltene Samples

For the analysis of five heavy oil/asphaltene samples for MW and MWD, same SEC systems used in retention time experiments (Section 2.1.1) were used.

Samples were dissolved in appropriate solvents. The solutions were filtered using micropore filter (Millipore Millex, pore size 0.45μm) prior to injection. Concentration of solution was ~ 0.85%.

A Spectra-Physics 4100 computing integrator equipped with Autolab GPC MWD software, Spectra-Physics MWD 5.0 (written in Basic) was used for data acquisition and reduction. The data system provided calibration of standards [log MW of standard vs retention time (retention time data from Waters data module used in retention time experiments, Section 2.1.1)], and for heavy oil/asphaltene samples, acquisition of MWD data in area slices, processing of the acquired data to calculate Mw, Mn and Mw/Mn (polydispersity), and MWD normalized and cumulative curves.

2.1.3 Determination of Molecular Weight and Intrinsic Viscosity

A Hitachi Perkin-Elmer Model 112 apparatus, and a GCL custom made apparatus were used for the determination of number average molecular weight of the five heavy oil/asphaltene samples by Vapour Pressure Osmometry (VPO) and Freezing Point Depression (FPD) methods respectively.

Intrinsic viscosity of heavy crudes/asphaltene samples in various solvents was determined by using a standard ASTM Cannon-Fenske Routine Viscometer, size number 50.

2.2 Description of Experimental Runs

2.2.1 Solvents

All solvents - o-Xylene, TCB, pyridine and THF used as SEC mobile phase were distilled in glass Burdick Jackson HPLC grade.

2.2.2 Model Compounds

The six classes of model compounds studied are presented in Table 1 with molecular weights shown in brackets. The model compounds used were either from the stock of standards at ORF laboratory or purchased from the following commercial sources: Beckman Instruments Canada Inc., Waters Associates, Varian, and Sigma Chemical Company.

2.2.3 SEC Columns and Equipment

See Details of Facilities in Section 2.1.

2.2.4 SEC of Model Compounds - Procedure

The SEC system used in this investigation is illustrated in Figure 2, and the chromatographic conditions and the data module parameter settings used are presented in Tables 2 and 3 respectively. The columns connected in series (in descending order of pore size for ultra styragel columns) were placed in Waters oven (Model TCM) set at temperatures selected for use in the study. Solvent was pumped by a reciprocating pump (Waters Model 6000A) at 0.1, 0.3 or 0.5 ml/min as required. Under working conditions, the pump delivered mobile phase at the selected flow rate with a stability better than ± 1%. Model compounds were dissolved in the mobile phase solvent and filtered when necessary using Waters Millex (0.45 μm)) filter unit. Injections were made by WISP loop auto injection system. The effluent detector was a Waters refractive index (Model 410) detector set at either 38°C or 50°C. The output signal of the detector was recorded on Waters data integration system (Model 730). All solvents used as the SEC mobile phase were distilled in glass Burdick Jackson HPLC grade and passed through a 2 μm filter before reaching the SEC column array.

2.2.5 SEC of Model Compounds - Experiments

A series of SEC experiments with model compounds were performed using the selected packings and solvents at various temperatures following the procedures described in Section 2.2.4 above. A listing of the experiments is shown in Table 4 and the retention time data presented in Tables 5 - 16.

2.3 Details of Methods

2.3.1 SEC Analysis of Heavy Crude Samples

The five heavy crude samples selected for MW and MWD analysis by SEC are identified as follows:

1. Lloydminster Heavy Oil
2. Cold Lake Heavy Oil
3. Visbreaking Residue
4. Visbreaking C_7 Asphaltene
5. Lloydminster C_7 Asphaltene

The above reference samples are from the stock of Energy Research Laboratories, CANMET, Ottawa.

Two systems - 1/ Zorbax PSM-60S in o-xylene at 35°C and 2/ Zorbax PSM-60S in THF at 35°C were used for the analysis of the heavy crude samples under similar SEC conditions used in model compound studies (Experiments XIII and XXI in Table 4). MW and MWD calculations were performed using calibration curves prepared from plots of retention time data against log MW of the model compounds. A Spectra-Physics 4100 computing integrator equipped with Autolab GPC MWD software, Spectra Physics MWD 5.0 was used for data acquisition and reduction (see Section 2.1.2, Details of Facilities - Analysis of Heavy Oil/Asphaltene Samples).

2.3.2 Determination of Molecular Weight of Heavy Crude Samples by Vapor Pressure Osnometry (VPO) Method

Sample Preparation

0.05 - 0.3g of asphaltene or 0.2 - 0.4g of pitch were weighed to 3 decimal places in a pre-weighed, capped vial. Benzene was added into the vial such that the total final mass of the solvent plus sample was 10g. This combined mass of solvent plus sample was also weighed to three decimals places. From this the grams of sample per combined kilograms solvent and sample was calculated.

Method

The operation of the Hitachi Perkin-Elmer Molecular Weight Apparatus is found in ref. 1. Approximately ½ ml of sample was washed over the thermistor in the apparatus. The thermistor was then washed with several drops of benzene solvent. Sample again was added dropwise until a stable Δ R value was observed. One drop of benzene was added through the reference cell and there was a delay of one minute before one drop of sample was added. The maximum Δ R value was taken if there was drifting in the needle on the apparatus. Δ R of the solvent alone was determined in the same manner and was subtracted from the sample Δ R. The moles of sample per total kg solvent plus sample were determined from a standard curve and the molecular weight was calculated by the formula:

$$MW = \frac{(\text{g sample})}{(\text{total kg})} \Big/ \frac{(\text{mol sample})}{(\text{ total kg })}$$

The Standard used was benzil with a molecular weight of 210.22.

The vapour pressure osmometry method produced very linear results (correlation coefficient = 1.0000) for a very wide range of standard concentrations (10^{-4} to 5×10^{-2} mol/kg). As well sample preparations were quick and easy. Disadvantages include the care required in handling benzene and inconsistant results when cyclohexane solvent was used with resins.

2.3.3 Determination of Molecular Weight of Heavy Crude Samples Freezing Point Depression (FPD) Method

Sample Preparation

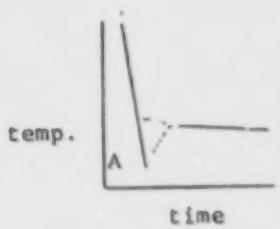
3g of pitch was weighed to three decimal places directly into a preweighed test tube. 50 ml of cyclohexane was pipetted into the test tube and the pitch was dissolved by mixing with a magnetic stir bar. 2-3g of dried barium chloride was added to absorb water. The samples were then frozen in the freezer and then thawed. This was repeated at least three times. Samples were stored in the freezer.

A sample of pure cyclohexane was prepared in the same manner.

Method:

The test tube was placed in a glass cylinder such that there was air between the test tube and the outside cylinder. A thermometer and a stirring rod were placed in the solution in the test tube. Then the cylinder and test tube were immersed in an ice bath. The stirring rod was activated to perform 120 up and down motions every minute. Temperature readings were taken every half minute until the drop in temperature was very slow. Then the temperature was read every 2 - 5 minutes for 10 minutes more. The apparatus was cleaned with methylene chloride and dryed between runs.

The freezing point of the sample was determined by plotting a graph of temperature versus time. An ideal plot is below.



The temperature at point A is the freezing point of the solution. Similarily the freezing point of pure solvent was determined. The difference between pure solvent freezing point and solvent with dissolved sample was the freezing point depression (D). Molecular mass was calculated by the formula:

$$M = ((F-D)WN)/DS$$

where W = sample weight (g)
N = solvent molecular weight
S = weight of solvent
M = molecular weight
F = solvent cryoscopic constant
D = freezing point depression

2.3.4 Determination of Intrinsic Viscosity ([n]) of Heavy Crude Samples and Polystyrene Standards in O-xylene

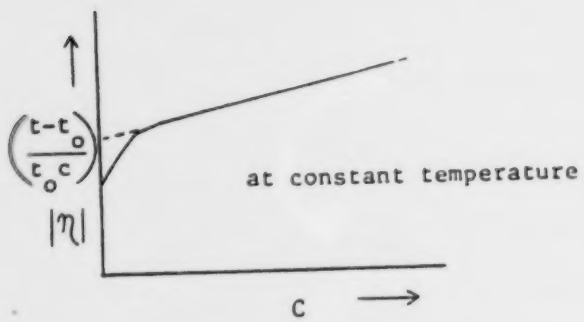
The general method of Brule (17) was followed for the determination of the intrinsic viscosity of pitch and asphaltenes in various solvents:

The viscometer used was a standard ASTM Cannon-Fenske Routine viscometer, size number 50. Specifications of the viscometer correspond to ASTM method D446-74.

Solutions of sample were prepared such that the time of flow between the marks on the viscometer did not exceed 1000 sec. From a series of sample solution, varying in concentration, a plot of $(t-t_o)/t_o c$ vs. c was made where:

t = time of flow of solution
t_o = time of flow of pure solvent
c = concentration of the solution

A typical curve was found as below:



The intrinsic viscosity, $[\eta]$, is related to the molecular weight, M, of the solute by the equation:

$$[\eta] = K M^a$$

where K and a are constants and can be determined by a plot of log n vs. log M from the standard molecules. The relationship of asphalt molecular weights to polystyrene molecular weights for intrinsic viscosity, was taken from Brule (17) and is given by:

$$\log M_{asphalt} = 3.21 - 1.04x + 0.331x^2$$

where x = log M polystyrene

The determinations of the flow times were done in triplicate and the average value was taken. All runs were done in a constant temperature water bath at 25.40°C. After the drainage time was determined on a particular solution, the viscometer was rinsed with methylene chloride and dried in an oven. The actual operating instructions of the viscometer was taken from ASTM method D445-83.

It should be noted that results for drainage times through the capillary became very inconsistent when dilute solutions were used for solutes of high molecular weight. This was due to fewer solute molecules contributing to the solute/solvent interactions that caused viscosity. Hence there was only a small sample of interactions which made up the average, overall intrinsic viscosity properties. Results for a solution of 10g of 35000 molecular weight polystyrene per kilogram of o-xylene varied up to 80 seconds with successive runs. Error bars on the plots for intrinsic viscosity show the maximum and minimum values from the 3 drainage times taken for each sample. (See Figures 33-35).

3. RESULTS AND DISCUSSION

3.1 Model Compound Study

As stated in the Introduction, the molecular weight determination of heavy crudes by SEC can be hampered by non-ideal elution patterns of various compound classes present in such samples. To simplify the study of elution behaviour, a series of model compounds representative of various compound classes present in heavy crudes was selected (see Table 1) and their elution studied in different solvents, packings and temperatures. A series of saturated hydrocarbons is included to represent non-polar molecules which should not be involved in hydrogen bonding and/or adsorption onto the column substrate. The PNA compounds studied included both condensed aromatics (3 ring or less) and highly condensed aromatics (> 3 ring), and contained molecules with alkyl substitution and molecules as large as coronene (300 MW). A series of N- and O-PNA was also examined to serve as representative of polar molecules which would be expected to show adsorptive properties involving the column substrate. Suitable high molecular weight N-PNA was not available, and only four N-PNA's e.g. two carbazoles and two acridines were used as model compounds. High molecular weight polystyrene standards of narrow MWD were used in order to simulate asphaltenes present in heavy crudes. Other polymers (polyethylenes, polyamides, polyesters, polyethylene glycols) as suggested in the RFP could not be used because of lack of availability of narrow MWD samples. In addition, these polymers showed poor solubility in the SEC solvents studied in the present work.

Elution behaviours of the model compounds were studied in two SEC systems - polystyrene gels and deactivated silica packings using different solvents (o-xylene, TCB, THF, and pyridine) and temperatures (35°, 60°, 90°, 120° and 140°C) and RI detector. (See list of experiments in Table 4). For each experiment, the elution times of the model compounds were recorded, and calibration data of twenty six (26) compounds (see Table 17) selected from thirty eight (38) model compounds studied were then used to construct curves in which the elution time is plotted against the log of the molecular weight. In addition, the calibration curves were prepared for

selected model compounds (8 PNA and 4 saturates - see Table 21) from runs in the two column packings in o-xylene and THF in which the elution time is plotted against the log of the respective bulk molar volumes values reported in the literature.

3.1.1 Polystyrene Gels

Initially, efficiency of separation of model compounds was studied on a set of 10^3Å + 100Å + 100Å Ultrastyragel columns (polystyrene gels) using o-xylene as the eluting solvent and the SEC conditions optimized (see Tables 2 and 3). The elution times from the above screening studies are presented in Tables 5-7. The results in Table 5 and 6 are from duplicate runs at 0.5mL/min flow rate at 35°C, and show good resolution of the model compounds. Also, the results show good reproducibility of the peak retention times. Results shown in Table 7 are from a similar run but performed at 60°C. Again, good resolution of the peaks is achieved and as expected, increasing the temperature is found to shift the peaks only slightly towards earlier elution.

Subsequent studies on polystyrene gels were performed with a new set of Ultrastyragel columns - 10^3Å + 500Å + 500Å connected in series. This switch was necessary since the 100Å Ultrastyragel packings used in the initial screening work could not be used at higher temperature (maximum temperature recommended for 100Å column: 60°C). With this new column system, the SEC conditions were again optimized and the reproducibility of the peak elution times were determined prior to final evaluation of the system in different solvents.

Retention time data of all model compounds studied in the above Ultrastyragel/o-xylene system at three temperatures (35°, 60° and 90°C) are presented in Table 8. Retention times of the twenty-six (26) selected model compounds at 35° and 90°C are shown in Table 17 (compiled from data in Table 8). Figures 3 and 4 illustrate the calibration curve/plots of log MW against retention times for the selected model compounds at 35° and 90°C

respectively. Log molar volume as well as log MW calibration plots of selected PNA and saturate model compounds from runs at 35°C are shown in Figure 14. Chromatographic profiles of each compound class model compounds at 60°C runs are presented in Figures 36 (A-F).

SEC studies of model compounds in the Ultrastyragel/o-xylene system have indicated the following:

1) Good resolution of each compound class model compounds is achieved (See SEC profiles in Figure 36).

2) The Polystyrenes (PS) and the saturates elute in the expected order with the largest molecule emerging first i.e. the retention time is related to the MW but this relationship is different for the polystyrenes and the saturates. As shown in the calibration curves in Figure 3, calibration is linear for both types of compounds, but with different slope. (Please note that only two calibration points for polystyrene model compounds have been used in constructing the curve. Calibration points of all polystyrene model compounds in Table 8 also gave a linear curve with same slope.) This has also been reported in literature in studies with polystyrene gel packings using THF, CH_2Cl_2 as eluting solvent.[15,16] Saturates used as model compounds are non-polar hydrocarbons and therefore no secondary interactions with the column substrate are anticipated. It is likely that some adsorption will be observed with PS model compounds due to interaction with polystyrene gel packings since both are aromatic. This effect is expected to be pronounced with the low molecular weight PS compounds, since adsorption is expected to be diminished with the increasing molecular weight. Retention time data of PS 955 and PS 570 in Table 8 show this. For example, PS 955 and PS 570 at 35°C run show retention times of 41.82 and 43.95 min respectively whereas the respective retention times of tristearin (MW 891), tripalmitin (MW 807) and n-octacosane (MW 395) are 39.90, 40.52 and 42.82 minutes. Similar trends are also seen at 60° and 90°C SEC runs.

3) The model PNA compounds exhibit anomalous SEC elution behaviour on polystyrene gels. This is clearly evident in the calibration

plots shown in Figures 3 and 4, and in retention time data in Table 8 which show that polynuclear aromatic compounds exhibit significantly higher retention times than predicted (compare the retention time of perylene, MW 252: 55.50 min with the retention time of n-octadecane, MW 254: 45.20 in o-xylene/35°C run. Similar differences in retention times of these two types of compounds are also observed at 60° and 90°C). This non-ideal elution of PNA compounds are attributed to their interaction with the polystyrene gel packing since both are aromatic.

4) Different elution patterns are observed even within the two PNA class of compounds studied. The retention time data of selected compounds in Table 17 show this. The less condensed PNA as a group (MW ranging between 156 and 192) are found to elute earlier than the highly condensed PNA group (MW between 202-300) indicating strong interaction of the highly condensed PNA with the gel. The calibration curves shown in Figures 3 and 4 indicate that the individual curves of the two PNA classes from both runs at 35° and 90°C are close to linear (with some points slightly out of line) with slopes steeper than those observed with PS and saturates.

5) The alkyl substituted PNA compounds e.g. 1,2-dimethyl naphthalene (156), 2,3,5-trimethyl naphthalene (170), 2-methyl phenanthrene (192), 9,10-dimethyl anthracene (206) and 9,10-dimethyl benzo[a]anthracene (256) are always found to elute at lower retention times than the unsubstituted PNAs. (See Table 8). This was true at all temperatures studied. This is to be expected not only because of their greater molar volume but also because of their higher solubility and because of a shielding effect (methyl substituents suppress the interaction of the aromatic ring with the gel), both of which minimize adsorption.

6) All N-PNA and O-PNA model compounds show significantly higher retention time than expected. This is shown in Tables 8 and 17. This is also reflected in the calibration plots in Figures 3 and 4. It is seen that there is considerable scatter and if curves are constructed from the calibration points, the corresponding curves will not be even remotely linear. The above

elution characteristics are attributed to interactions between these polar molecules and the polystyrene gel resulting in adsorption and/or partition which is enhanced by their poor solubility in o-xylene.

7) Temperature is found to have little effect on the elution behaviour of the model compounds. Increasing the temperature shifts the peaks only slightly toward earlier elution.

8) Use of bulk molar volume (product of density and molecular weight) as the effective size parameter instead of molecular weight shows no differences in the elution patterns of twelve (12) model compounds studied. This is shown in the two calibration curves in Figure 14. Both molar volume and molecular weight curves show quite similar calibration. Twelve model compounds were selected because the molar volume data of only these compounds are available in the literature.

In order to determine whether significant improvements in the elution behaviour can be achieved, two other solvents - 1,2,4-trichlorobenzene (TCB) and THF were studied as SEC eluent.

Retention time data of all model compounds in the Ultrastyragel/TCB system at four temperatures (60°, 90°, 120° and 140°C) are presented in Table 9, and data for the twenty-six (26) selected compounds at 90° and 140°C are shown in Table 17 (compiled from data in Table 9). Figures 5 and 6 illustrate the calibration curve/plots of log MW against retention times of the selected model compounds at 90° and 140°C respectively.

The elution patterns of the model compounds are found quite comparable with those observed in o-xylene except that saturates and the polystyrenes now fall in one line and the PNA calibration is slightly less steeper in TCB. The calibration points for N-PNA and O-PNA compounds show considerable scatter

indicating strong interactions of these polar compounds with the polystyrene gels. The claim that TCB can practically eliminate the differences in elution behaviour resulting in a linear calibration of saturates and condensed polynuclear aromatics[8,9] (See Figure 1) could not be substantiated in the present study.

Studies with THF, the widely used eluent in SEC analysis of heavy crudes have also shown no improvements in the elution behaviour of model compounds.

Retention time data of all model compounds in the Ultrastyragel/THF system at 35°C are given in Table 10. Retention time data for the twenty-six (26) selected compounds are presented in Table 17 (compiled from data in Table 10), and their log MW calibration curves/plots shown in Figure 7. Log MW and molar volume calibration of selected PNA and saturates are given in Figure 16.

In THF, the elution patterns of the model compounds with the exception of N- and O-PNA are found almost identical to those observed in o-xylene (compare calibration curves in Figures 3 and 7 and in Figures 14 and 16). Other researchers have also reported similar anomalous elution behaviour in THF.[7,8]

The N- and O-PNA model compounds studied also show longer retention times than expected, but they are found to elute at retention times much faster than observed in o-xylene and TCB. This indicates two things:

1) solute-gel interactions of the model compounds which result in delayed elution due to adsorption, and

2) solute-solvent interactions e.g. hydrogen bonding between THF and the polar functionalities in N- and O-PNA effectively producing a molecule which exhibits a greater linear molecular size, and therefore a smaller retention time.

Our studies with the model compounds on polystyrene gels have shown that the anomalous retention behaviour of the PNA compound types are not eliminated in the three solvents examined. It is concluded that the polystyrene gels may not be the appropriate SEC packings for determining the heavy crude MW distribution since the suppression of the interaction of the PNA with the gels are not achieved and the data of the model compounds are not correlated onto a single calibration line.

3.1.2 Deactivated Silica Packings

Another packing studied in the present work is the rigid silica-based packings (silanized Zorbax PSM 60-S from Dupont), surface of which have been deactivated to eliminate adsorption effects by silylation with chlorotrimethylsilane. Studies with the above packings were performed in four solvents - o-xylene, TCB, pyridine and THF. Results of retention time experiments are recorded as follows:

SEC runs in o-xylene/PSM 60-S system were carried out at 0.5 mL/min. at 35°C and at 0.3 mL/min flow rates at 35°, 60° and 90°C. For runs at 0.5 mL/min. flow rate, retention time data for all model compounds are shown in Table 11, and data for 26 selected compounds and their MW calibration curve/plots are shown in Table 18 (compiled from Table 11) and Figure 8 respectively. For runs at 0.3 mL/min flow rate, retention time data for selected model compounds at 35°C, are tabulated in Table 12 and for all model compounds at 35°C, 60° and 90°C are tabulated in Table 13; data and MW calibration of 26 selected compounds for 35° and 90°C are presented in Table 19 (compiled from Table 13) and Figures 9 (35°C) and 10 (90°C) respectively; bulk molar volume and MW curves for selected PNA and saturates are shown in Figure 15. Typical chromatographic profiles of some compound classes of model compounds from runs at 0.3 mL/min. at 35°C are shown in Figure 37 (A-D).

Retention time experiments in TCB were performed at 0.1 mL/min. at three temperatures (35°, 60° and 90°C) and in pyridine at 35°C also at 0.1 mL/min. flow rate. TCB retention time data at the three temperatures are presented in Table 14, and data for 26 selected compounds and their MW calibration curves/plot for run at 90°C are given in Table 20 (compiled from Table 14) and Figure 11 respectively. Data for all model compounds in pyridine are recorded in Table 15, and data and MW calibration for the 26 selected compounds are given in Table 20 (compiled from Table 15) and Figure 12 respectively.

SEC runs in THF was performed at 35°C at 0.3 mL/min. flow rate. Table 16 shows the retention time data of all model compound, and the data for

26 selected model compounds and their MW calibration are presented in Table 19 (compiled from Table 16) and Figure 13 respectively. Molar volume and MW calibration of selected PNA and saturates are presented in Figure 17.

The above SEC studies of the model compounds on PSM 60-S deactivated silanized silica packings in the four solvents have inidicated the following:

1) In all solvents studied with the two column PSM 60-S SEC system, noticeable differences in retention times within each compound class type of model compounds have been observed. Reproducibility studies have substantiated this.

2) In o-xylene studies, all model compounds with the exception of N- and O-PNA show near ideal elution behaviour indicating very little adsorption/partitioning of these compounds on the silanized silica packings. Calibration curves in Figures 8 - 10 show this, where the data for most of the model compounds correlate onto a single calibration line. Data from runs at different flow rate and at different temperatures substantiate this. Whether deviation of the N- and O-PNA from ideal elution behaviour is due to their adsorption/partitioning on the packings is not known. High temperature runs at 60°C (see data in Table 13) and 90°C (see data in Table 13 and calibration in Figure 10) tend to bring the two N-PNA e.g. carbazole and dibenzcarbazole and the two O-PNA e.g. pyrene-and phenanthrene carboxaldehyde into calibration.

3) In TCB runs, the polystyrene (PS) and the saturate model compound are found to elute in the expected order with the largest molecule emerging first. This is also true with most of the compounds in the PNA group. Calibration curve shown in Figure 11 for the 90°C run show that the PS and the PNA fall on a single line. Calibration is also linear for the saturates but with a different slope. The worst case was observed with the N- and O-PNA. Acridines and most of the O-PNA are either not eluted or elute at

longer retention time indicating strong adsorption/partitioning effect on the packing. Temperature is found to minimize this effect for the two carbazoles (see data in Table 14 and calibration in Figure 11 for runs at 90°C).

4) In pyridine studies, the model compounds within each compound type class with a few exceptions in the PNA group elute in the expected order i.e. retention time is related to molecular weight, but the relationship is different for each compound class. For instance, the polystyrenes and the saturates - both give linear calibration but with a different slope (see calibration curves in Figure 12). The data of the PNA class of compound including the N- and O-PNA are close to correlation to a single curve with considerable scatter but with a slope which is different from slopes observed with polystyrenes and saturates. The unusual retention behaviour of the polystyrene and the saturates is probably due to adsorption on the packing which is strongly influenced by solvent polarity. The near ideal elution behaviour of the polar PNA model compounds may be related to the polarity of the pyridine solvent.

5) In THF runs, all model compounds with the exception of O-PNA show near ideal elution behaviour. This is shown in the linear calibration curve in Figure 13. All data points (excluding the data for tristearin and tripalmitin) are seen to correlate fairly well onto a single calibration line with some scatter. It is interesting to note that the four O-PNA studied show slightly shorter retention time than observed with other PNA (see Table 19 and Figure 13). This is probably due to solute-solvent interactions e.g. hydrogen bonding between THF and the polar functionalities present in O-PNA model compounds.

6) Use of bulk molar volume as the effective size parameter instead of molecular weight shows no difference in the elution pattern of model compounds. This is shown in the calibration curves in Figures 15 and 17. Both molar volume and molecular weight curves show quite similar calibration for some selected PNA and saturate compound.

The above studies have indicated that adsorption/partitioning (so-called secondary effects) of various classes of model compounds can be minimized or prevented when SEC is performed in o-xylene/Zorbax PSM-60-S or in THF/Zorbax PSM 60-S systems. It has been demonstrated that with such systems, MW/retention time data for all but a few compounds e.g. acridines, O-PNA correlate fairly well to a single calibration line. These two systems were therefore selected over other column/solvent combinations for determining molecular weight and molecular weight distribution of the heavy crude samples.

3.2 SEC Analysis of Heavy Crude Samples

The five heavy oil/asphaltene samples were analyzed for determination of MW distribution under two SEC conditions:

1) o-xylene-Zorbax PSM 60-S system at 35°C at 0.3 mL/min flow rate

2) THF-Zorbax PSM 60-S system at 35°C at 0.3 mL/min flow rate.

3.2.1 o-Xylene-PSM 60-S System

For calibration, two sets of data were used -

1) Data of 22 model compounds and the calibration curve shown in Table 12 and Figure 18 respectively

2) Data of 25 model compounds and the calibration curve shown in Table 13 and Figure 19 respectively.

The samples were analysed under similar SEC conditions used for model compounds studies. The chromatographic profiles and the normalized/cumulative MWD curves of the samples are shown in Figures 20-24 (Figure 20 - Cold Lake heavy oil; Figure 21 - Lloydminster heavy oil; Figure 22 - Visbreaking residue; Figure 23 - Visbreaking C_7 asphaltene; Figure 24 - Lloydminster C_7 asphaltene). For calibration, a linear calibration fit (Figure 18) was used

for Cold Lake and Lloydminster heavy oil samples and a cubic fit (Figure 19) was used for the analysis of the other three samples.

The MW and MWD results of analysis of the heavy crude samples are shown in Table 22.

3.2.2 THF-PSM 60-S System

For calibration, data of model compounds shown in Table 16 were used. The following calibration procedure was followed:

1) Linear and cubic fit calibration of model compounds in Table 16 (excluding PS 42,800) shown in Figure 25;

2) Linear and cubic fit calibration of model compounds in Table 16 (excluding pyrene carboxaldehyde, phenanthrene quinone, phenanthrol, hydroxy fluorene, acridine and carbazole) shown in Figure 26; and linear and cubic fit calibration of model compounds in Table 16 (excluding the above six and PS 42,800) shown in Figure 27.

The samples were analyzed under similar SEC conditions used for model compound studies. The chromatographic profiles and the normalized/cumulative MWD curves of the samples are shown in Figures 28-32 (Figure 28 - Cold Lake heavy oil; Figure 29 - Lloydminster heavy oil; Figure 30 - Visbreaking residue; Figure 31 - Visbreaking C_7 asphaltene; Figure 32 - Lloydminster C_7 asphaltene).

The MW and MWD results of analysis of the heavy crude samples and the calibration fit used are shown in Table 23.

SEC studies of heavy crude samples on deactivated silica packings have shown the following:

1) With polysterene gels in THF, CH_2Cl_2 and other solvents, heavy crudes and in particular their asphaltene fractions show a prominent tail. Adsorption of the low molecular weight PNA compounds present in heavy crudes usually causes this tailing. But in this work with PSM 60-S/THF/o-xylene system, this tail is almost completely eliminated. This is shown in the SEC

profiles of the samples. The elimination of the tail in the systems studied may be attributed to the near ideal elution patterns of the PNA in o-xylene and THF, similar to that observed in model compound studies.

2) In general, the heavy crudes and their asphaltene fractions during SEC on polystyrene gels in THF, CH_2Cl_2 or other solvents give rise to asymmetric/bi-modal curve, in which a narrow high molecular size component is superimposed on a broad lower molecular weight component. In contrast, the SEC elution curves of the samples analysed on silanized silica packings are Gaussian or quasi Gaussian indicative of a homogenous molecular size distribution. The profiles also show that the curves for asphaltenes e.g. Lloydminster asphaltene fractions result from much higher molecular weight species (lower retention times) than are present in the non-polymeric sample e.g. Visbreaking residue.

3) Polydispersity, the ratio of the Mw to Mn indicates a much wider distribution of molecular sizes in the Lloydminster heavy oil asphaltene and a wider distribution in the parent heavy oil compared to distribution observed with Visbreaking residue and its asphaltene fraction. This was expected.

4) Good correlations in MW and MWD values between the two solvents are obtained (see Tables 22 and 23), particularly for the Cold Lake heavy oil, Visbreaking residue and its C_7 asphaltene. Slightly higher values in THF are probably due to greater solubility of the high molecular components of the samples in THF than in o-xylene.

3.3 Limitation of the SEC Method

The dual column PSM 60-S used for the separation was studied using model compounds representative of various types. In o-xylene and THF, all model compounds with the exception of N- and O- PNA showed near ideal elution behaviour on the silanized silica packings. Deviation of the N- and O- PNA compounds from ideal elution behaviour suggests the SEC method may not be applicable for determining molecular weight distribution of heavy crudes, e.g. coal liquids, coal-bitumen co-processed liquids. These samples are known to contain high concentrations of oxygenated compounds.

Use of suitable reference compounds as calibration standards is important in order to realize the full potential of the SEC system. Whether the model compounds used in the present study represent compound types present in heavy crudes, and are realistic calibration standards are not known. Only a limited molecular weight range of known PNA and N- and O- PNA heterocyclic is available. There are very few compounds with molecular weight above 300 (coronene) which can serve as suitable reference standards for heavy crudes. Since many heavy crudes/asphaltenes contain high concentrations of compounds with molecular weights considerably in excess of 300, it is not possible to obtain calibration standards for the higher molecular weight ranges. Even for the compounds in the low molecular weight range, there are very few methylated PNA and N- and O- PNA compounds available for the study.

3.4 Comparison Between SEC & Other Molecular Weight Methods

A preliminary estimate of the accuracy of the SEC method has been made by comparing the SEC Mn values of the heavy crude samples with those obtained by vapour pressure osmometry (vpo) and freezing point depression (fpd) molecular weight measurements.

The number average molecular weights of the samples were measured by vpo in both benzene and o-xylene, and by fpd in cyclohexanone. All five samples were analysed by vpo in benzene; but in o-xylene, all samples except the Llyodminster asphaltene were analysed. The Mn values of only two heavy oil samples - Cold Lake and Llyodminster samples were determined by fpd technique. In general, problems were encountered in the analysis of asphaltene samples in both techniques. The results are shown in Table 24. The weight average molecular weight (Mw) of the samples by light scattering technique could not be determined because of lack of available facilities. The intrinsic viscosities were determined for three heavy oil samples, and the results are presented in Table 24.

The results have shown the following:

1) A fairly good agreement in Mn values for the Llyodminster and Cold Lake heavy oil samples is obtained between the vpo and fpd methods.

2) Runs in benzene and o-xylene show good correlations in vpo Mn values for the three samples - the two heavy oils and the visbreaking residue.

3) Satisfactory correlation between the SEC and the vpo/fpd Mn values is not achieved (compare the SEC Mn values in Tables 22 and 23 with the vpo/fpd values in Table 24). This discrepancy is explained as follows: (a) Consistently high Mn values are observed for all samples in vpo/fpd measurements. This is also seen with the two pure standards, e.g. pyrene and n-octacosane (see Table 24). The heavy crude samples and their fractions are quite polar and it is possible that they exhibit molecular association and/or hydrogen bonding in non-polar solvents, e.g. o-xylene, benzene, resulting in an increase in the apparent average molecular weight. (b) Error in SEC Mn values may also be attributed to lack of correlations between the SEC retention time and molecular weight for the lower molecular weight components of heavy crudes. This suggests the application of suitable well characterized heavy crude type low molecular weight reference compounds for calibration purposes. (c) Mn results are known to be influenced by solvent type and solute concentration in vpo measurement technique. Generally, high solute concentrations used are responsible for erroneous results. It is known that vpo in THF show a decrease in MW value while vpo in benzene show an unexpected increase in MW[15]. These problems in vpo measurement should be addressed.

Intrinsic viscosity were measured for some samples. Due to lack of suitable polymer standards of different types, solubility problems and difficulty in calculating hydrodynamic volume the results could not be applied. Furthermore, the calculation of molecular weight using Brule (17) equation required the determination of constants a and K from a series of polymer standards of the sample type which were difficult to obtain. These aspects were discussed with scientific authority.

4. REFERENCES

1. J.G. Hendrickson and J.C. Moore, J. Poly. Sci. Part A, 4, 167-168 (1966).

2. G.D. Edwards and Q.Y. Ng, J. Poly. Sci. Part C, 21, 105-117 (1968).

3. J.G. Hendrickson, Anal. Chem. 40, 49-53 (1968).

4. J. Cazes and D. Gaskill, Sep. Sci. 2, 421-430 (1967).

5. W.B. Smith and A. Kollmansberger, J. Phy. Chem. 69, 41576-4161 (1965).

6. J. Cazes and D. Gaskill, Sep. Sci. 4, 15-24 (1969).

7. H.H. Oelert, D.R. Latham and W.E. Haines, Sep. Sci. 5, 657-668 (1970).

8. J.G. Bergman, L.J. Duffy and R.B. Stevenson, Anal. Chem. 43, 131-133 (1971).

9. J.G. Bergman, L.J. Duffy and R.B. Stevenson, Preprints, ACS, Division of Petroleum Chemistry, vol. 5, No. 1.2, February 22-27, (1970), A 217-224.

10. J.H. Weber and H.H. Oelert, Sep. Sci. 5, 669-675 (1976).

11. A. Majid and J. Woods, Preprints, ACS, Division of Fuel Chemistry, April 8-13, 176-178 (1984).

12. T. Edstrom and B.A. Petro, J. Poly. Sci. Part C, 21 171-182 (1968).

13. K.H. Algeit and T.H. Gouw, "Chromatography of Heavy Petroleum Fractions," in Advances in Chromatography, 13, 132 (1975).

14. L.R. Snyder, Anal. Chem. 41, 1223-1227 (1969).

15. P.J. Champagne, E. Manolakis and M. Ternan, Fuel, 64, 423-425 (1985).

16. K.D. Bartle, M.J. Mulligan, N. Taylor, T.G. Martin and C.E. Snape, Fuel, 63, 1556-1560 (1984).

17. B. Brule, Am. Chem. Soc. Div. Fuel Chem. Prepr. 26(2), 28-37 (1981).

TABLES 1-24

TABLE 1

List of Model Compounds Used

Polystyrenes

- MW 30,100
- MW 9,000
- MW 4,000
- MW 2,000
- MW 955
- MW 570

PNA of Low Condensation (3 ring or less)

- (206) 9,10-DiMe Anthracene
- (192) 2-Me Phenanthrene
- (178) Phenanthrene
- (170) 2,3,5-TriMe Naphthalene
- (166) Fluorene
- (156) 1,2-DiMe Naphthalene

Condensed PNA (> 3 rings)

- (300) Coronene
- (278) Dibenz[ah]Anthracene
- (276) Benz[ghi]Perylene
- (256) DMBA
- (252) Perylene
- (228) Chrysene
- (202) Pyrene

N-PNA

- (281) Dibenz[ai]Acridine
- (267) 13 H Dibenzo[ai]Carbazole
- (179) Acridine
- (167) Carbazole

O-PNA/Fatty Acid

- (288) Pyrene butyric acid
- (284) Stearic acid
- (252) Anthraquinone Carboxylic Acid
- (230) Pyrene Carboxaldehyde
- (226) Hydroxy Fluorene Carboxylic Acid
- (208) Phenanthraquinone
- (206) Phenanthrene Carboxaldehyde
- (194) Phenanthrol
- (182) Hydroxy Fluorene

Saturates

- (891) Tristearin
- (807) Tripalmitin
- (395) n-Octacosane
- (283) n-Eicosane
- (254) n-Octadecane
- (226) n-Hexadecane

TABLE 2

SEC Chromatographic Conditions

Instrument	:	Waters HPLC pump system
Column	:	10^3Å + 500Å + 500Å Ultrastyragel or 2 x Zorbax PSM 60-S columns in series
Column Temperature	:	35°C, 60°C, 90°C, 120°C and 140°C
Flow Rate	:	0.1, 0.3 and 0.5 mL/min.
Detector	:	Waters RI 410
Detector Temperature	:	38°C or 50°C
Detector Sensitivity	:	64
Detector Scale Factor	:	2
Detector Time Constant	:	3
Detector Polarity	:	Positive (negative with saturates model compounds)
Data Handling	:	Waters Data Control Module
Injection	:	20 - 100 µL (WISP Auto Sampler)
Concentration	:	0.6 - 0.8% in appropriate solvent for model compounds and ~ 0.85% for heavy crude samples

TABLE 3

Data Control Module Peak Parameter Settings

00	08/10/86	DATE
01	16:16:39	TIME
02	0.15	CHART SPEED, cm/min
03	OFF	PLOT
04	OFF	PEN 2
05	10	PEN 1 ZERO
06	90	PEN 2 ZERO
07	ON	AUTO ZERO
08	LC	GPC/LC
09	ON	CALIB
20	OFF	AUTO PARAMETER
21	20	PEAK WIDTH
22	500	NOISE REJECTION
23	100	AREA REJECTION
24	100.00	RUN STOP

PEAK #	RT	AMOUNT

TABLE 4

List of SEC Experiments with Model Compounds

Sec Run #	Column Type	Solvent Type	Column Temp (°) Detector 50°C	Flow Rate (mL/min)	Retention Time of all Model Compounds (min)	Retention Time & Calibration of 26 Selected Model Compounds		SEC Profiles
						Retention Time (min)	Calibration Curves	
I	Ultrastyragel 10^3Å+100Å+100Å	o-Xylene	35°C (Detector: 38°C)	0.5	Table 5	-	-	-
II (Repeat of I)	Ultrastyragel 10^3Å+100Å+100Å	o-Xylene	35°C (Detector: 38°C)	0.5	Table 6	-	-	-
III	Ultrastyragel 10^3Å+100Å+100Å	o-Xylene	60°C (Detector: 50°C)	0.5	Table 7	-	-	-
IV	Ultrastyragel 10^3Å+500Å+500Å	o-Xylene	35°C (Detector: 38°C)	0.5	Table 8	Table 17	Figure 3	-
V	Ultrastyragel 10^3Å+500Å+500Å	o-Xylene	60°C (Detector: 35°C)	0.5	Table 8	-	-	Figure 36
VI	Ultrastyragel 10^3Å+500Å+500Å	o-Xylene	90°C (Detector: 35°C	0.5	Table 8	Table 17	Figure 4	-
VII	Ultrastyragel 10^3Å+500Å+500Å	TCB	60°C	0.5	Table 9	-	-	-
VIII	Ultrastyragel 10^3Å+500Å+500Å	TCB	90°C	0.5	Table 9	Table 17	Figure 5	-
IX	Ultrastyragel 10^3Å+500Å+500Å	TCB	120°C	0.5	Table 9	-	-	-
X	Ultrastyragel 10^3Å+500Å+500Å	TCB	140°C	0.5	Table 9	Table 17	Figure 6	-

Continued . . .

TABLE 4 (Cont'd.)

List of SEC Experiments with Model Compounds

Sec Run #	Column Type	Solvent Type	Column Temp (°) Detector 50°C	Flow Rate (mL/min)	Retention Time of all Model Compounds (min)	Retention Time & Calibration of 26 Selected Model Compounds		SEC Profiles
						Retention Time (min)	Calibration Curves	
XI	Ultrastyragel 10^3Å+500Å+500Å	THF	35°C (Detector: 38°C)	0.5	Table 10	Table 17	Figure 7	-
XII	2 x Zorbax PSM 60 S	o-Xylene	35°C (Detector: 38°C)	0.5	Table 11	Table 18	Figure 8	-
XIII	2 x Zorbax PSM 60 S	o-Xylene	35°C (Detector: 38°C)	0.3	Table 12	-	-	-
XIV	2 x Zorbax PSM 60 S	o-Xylene	35°C (Detector: 38°C)	0.3	Table 13	Table 19	Figure 9	Figure 37
XV	2 x Zorbax PSM 60 S	o-Xylene	60°C (Detector: 35°C)	0.3	Table 13	-	-	-
XVI	2 x Zorbax PSM 60 S	o-Xylene	90°C (Detector: 35°C	0.3	Table 13	Table 19	Figure 10	-
XVII	2 x Zorbax PSM 60 S	TCB	35°C (Detector: 38°C)	0.1	Table 14	-	-	-
XVIII	2 x Zorbax PSM 60 S	TCB	60°C (Detector: 35°C)	0.1	Table 14	-	-	-
XIX	2 x Zorbax PSM 60 S	TCB	90°C (Detector: 35°C)	0.1	Table 14	Table 20	Figure 11	-
XX	2 x Zorbax PSM 60 S	Pyridine	35°C	0.1	Table 15	Table 20	Figure 12	-
XXI	2 x Zorbax PSM 60 S	THF	35°C	0.3	Table 16	Table 19	Figure 13	-

WI·SP SAMPLE IDENTIFICATION RECORD

Run Identification: TABLE 5 **Date** 4,5,6 Oct, '86

Analysis: Retention Time Data **Carriage No.** _____

Ultrastyragel(10^3Å+100Å+100Å)/o-Xylene/35°C/0.5 mL/min **Operator** _____

Analysis Conditions

Column 10^3Å+10^2Å+10^2Å **I.D.#** Ultrastyragel

Detector Waters RI 410 @ 38°C

Eluent o-Xylene @ 0.5 mL/min @ 35°C

Detector Sens: 64
Scale Factor : 2
Time Constant: 3

100 µL Injection
85 min Run Time
5 min Eq. Delay

No.	Inj. Vol.	No. of Injs.	Ret. Time (min)	Sample Identification	No.	Inj. Vol.	No. of Injs.	Ret. Time (min)	Sample Identification
1			32.15	PS Std MW 15000	25			36.15	Tripalmitin (807)
2			32.22	PS Std MW 9000	26			38.52	n-octacosane (395)
3			33.32	PS Std MW 4000	27			40.72	n-eicosane (283)
4			35.02	PS Std MW 2000	28			41.47	n-octadecane (259.5)
5			38.00	PS Std MW 955	29			42.35	n-hexadecane (226.5)
6			40.80	PS Std MW 570	30			55.15	Phenanthrene (178)
7			53.35	9,10-DiMe Anthracene (206)	31			55.17	Dibenz[ah]A (278.4)
8			53.70	2-Me Phenanthrene (192	32			55.20	Benz[ghi]Per (276.3)
9					33				
10			51.80	2,3,5-TriMe Naph (170	34				
11			53.95	Fluorene (166)	35				
12			52.75	1,2-Di-Me Naph (156)	36				
13			56.12	Coronene (300)	37				
14					38				
15					39				
16			52.75	DMBA (256.3)	40				
17			55.95	Perylene (252)	41				
18			54.57	Chrysene (228.3)	42				
19			55.82	Pyrene (202.3)	43				
20			59.12	Dibenz[ai]acridine(281)	44				
21			62.85	DibenzCarbazole(267.3)	45				
22			63.60	Acridine (179)	46				
23			59.65	Carbazole (167)	47				
24			35.60	Tristearin (891)	48				

Notes

WI-SP™ SAMPLE IDENTIFICATION RECORD

Run Identification: TABLE 6 Date 6,7 / Oct. / '86

Analysis: Retention Time Data Carriage No. _____

Ultrastyragel(10^3+100Å+100Å)/o-Xylene/35°C/0.5 mL/min Operator _____

(Repeat of Experiment run in Table 5)

Analysis Conditions

Column 10^3Å+10^2Å+10^2Å I.D.# Ultrastyragel

Detector Waters RI 410 @ 38°C

Eluent o-Xylene @ 0.5 mL/min @ 35°C

Detector Sens: 64
Scale Factor : 2
Time Constant: 3

100 µL Injection
85 min Run Time
5 min Eq. Delay

No.	Inj. Vol.	No. of Injs.	Ret. Time (min)	Sample Identification	No.	Inj. Vol.	No. of Injs.	Ret. Time (min)	Sample Identification
1			29.22	PS Std MW 30,100	25			40.22	n-eicosane (283)
2			31.67	PS Std MW 15,000	26			41.57	n-octadecane (254.5)
3			31.65	PS Std MW 9,000	27			41.95	n-hexadecane (226.5)
4			33.05	PS Std MW 4,000	28			54.52	Phenanthrene (178)
5			34.72	PS Std MW 2,000	29			52.97	Dibenz[ah]A (278.4)
6			37.72	PS Std MW 955	30			55.45	Benz[ghi]Per (276.3)
7			40.15	PS Std MW 570	31			ND	1-Pyrene Butyric Acid (288)
8			52.50	9,10-DiMe Anthracene (206)	32			ND	Anthraquinone 2-Carboxylic Acid (252)
9			52.85	2-MePhenanthrene (192)	33			54.45	1-Pyrene Carboxaldehyde (230)
10			50.80	2,3,5-TriMe Naph (170)	34			ND	9-Hydroxy 9-Fluorene COOH (226)
11			54.82	Fluorene (166)	35			53.35	Phenanthraquinone (208)
12			52.62	1,2-DiMe Naph (156)	36			53.62	Phenanthrene 9-Carboxaldehyde (206)
13			55.75	Coronene (300)	37			68.45	9-Phenanthrol (194)
14			52.25	DMBA (256.3)	38			56.55	9-Hydroxy Fluorene (182)
15			54.82	Perylene (252)	39			ND	Stearic Acid (284)
16			53.50	Chrysene (228.3)	40				
17			54.60	Pyrene (202.3)	41				
18			58.05	Dibenz[ai]acridine (281)	42				
19			61.52	DibenzCarbazole (267.3)	43				
20			62.15	Acridine (179)	44				
21			58.02	Carbazole (167)	45				
22			34.65	Tristearin (891)	46				
23			35.72	Tripalmitin (807)	47				
24			37.97	n-octacosane (395)	48				

Notes

WI·SP™ SAMPLE IDENTIFICATION RECORD

Run Identification: TABLE 7

Date 10,11,12 Oct. '86

Analysis: Retention Time Data

Carriage No. _____

Ultrastyragel(10^3+100Å+100Å)/o-Xylene/60°C/0.5 mL/min

Operator _____

Analysis Conditions

Column 10^3Å+10^2Å+10^2Å I.D.# Ultrastyragel

Detector Waters RI 410 @ 50°C

Eluent o-Xylene @ 0.5 mL/min @ 60°C

Detector Sens: 64
Scale Factor : 2
Time Constant: 3

100 µL Injection
85 min Run Time
5 min Eq. Delay

No.	Inj. Vol.	No. of Injs.	Ret. Time (min)	Sample Identification	No.	Inj. Vol.	No. of Injs.	Ret. Time (min)	Sample Identification
1			28.50	PS Std MW 30,100	25			53.72	Pyrene Carboxaldehyde(230)
2			31.10	PS Std MW 15,000	26			52.90	Phenanthraquinone (208)
3			31.10	PS Std MW 9,000	27			52.82	Phenanthrene 9-Carboxaldehyde (206)
4			32.45	PS Std MW 4,000	28			63.60	Phenanthrol (194)
5			34.02	PS Std MW 2,000	29			55.27	Hydroxy Fluorene (182)
6			36.90	PS Std MW 955	30			35.17	Tristearin (891)
7			-	PS Std MW 570	31			35.70	Tripalmitin (807)
8			51.15	9,10-DiMeAnthracene(206)	32			38.15	n-octacosane (395)
9			51.45	2-MePhenanthrene(192)	33			40.35	n-eicosane (283)
10			52.85	Phenanthrene (178)	34			41.02	n-octadecane (254.5)
11			49.87	2,3,5-TriMe Naph(170)	35			41.90	n-hexadecane (226.5)
12			51.92	Fluorene (166)	36				
13			50.82	1,2-DiMe Naph (156)	37				
14			53.87	Coronene (300)	38				
15			52.15	Dibenz[ah]A (278)	39				
16			54.20	Benz[ghi]Per (276)	40				
17			51.35	DMBA (256) .	41				
18			54.15	Perylene (252)	42				
19			53.00	Chrysene (228)	43				
20			54.22	Pyrene (202)	44				
21			55.45	Dibenz[ai]acridine(281)	45				
22			58.65	Dibenz Carbazole (267)	46				
23			59.35	Acridine (179)	47				
24			57.80	Carbazole (167)	48				

Notes

TABLE 8

Effect of Temperature on Retention Time of Model Compounds
(SEC Conditions: 10^3Å + 500Å + 500Å Ultrastyragel
Column in Series; o-Xylene as Solvent @ 0.5 mL/min

Model Compounds	Retention Time (min)		
	35°C	60°C	90°C
Polystyrenes			
MW 30,100	28.80	28.35	27.92
MW 9,000	33.42	33.07	32.42
MW 4,000	36.22	35.72	35.10
MW 2,000	38.52	38.00	37.80
MW 955	41.82	41.27	40.40
MW 570	43.95	43.35	42.42
PNA (3 ring or less)			
(206) 9,10-DiMe Anthracene	53.10	52.22	50.90
(192) 2-Me Phenanthrene	53.50	52.65	51.07
(178) Phenanthrene	54.50	53.70	52.12
(170) 2,3,5-TriMe Naph	51.97	51.40	49.95
(166) Fluorene	53.52	52.82	51.42
(156) 1,2-DiMe Naph	52.60	51.65	50.52
PNA (4 ring or more)			
(300) Coronene	55.42	54.17	52.80
(278) Dibenz[ah]A	53.55	52.45	51.15
(276) Benz[ghi]Per	55.72	54.45	52.81
(256) DMBA	55.82	51.87	50.42
(252) Perylene	55.50	54.20	52.77
(228) Chrysene	54.30	53.17	51.87
(202) Pyrene	55.05	53.82	52.60
N-PNA			
(281) Dibenz[ai]Acridine	63.12	58.42	55.87
(267) Dibenz Carbazole	65.65	61.07	58.02
(179) Acridine	68.75	62.42	59.07
(167) Carbazole	60.32	58.20	56.50
O-PNA			
(230) Pyrene Carboxaldehyde	55.42	54.15	53.17
(208) Phenanthraquinone	55.25	54.05	53.47
(206) Phenanthrene Carboxaldehyde	54.57	53.40	52.40
(194) Phenanthrol	73.90	66.70	62.50
(182) Hydroxy Fluorene	59.27	56.65	55.07
Saturates			
(891) Tristearin	39.90	39.27	38.67
(807) Tripalmitin	40.52	39.95	39.30
(395) n-Octacosane	42.82	42.15	41.47
(283) n-Eicosane	44.55	43.90	43.17
(254) n-Octadecane	45.20	44.47	43.72
(226) n-Hexadecane	45.77	45.12	44.27

TABLE 9

Effect of Temperature on Retention Time of Model Compounds
(SEC Conditions: 10^3Å = 500Å + 500Å Ultrastyragel
Columns in Series: 1,2,4-TCB as solvent @ 0.5 mL/min)

Model Compounds		Retention Time (min)			
		60°C	90°C	120°C	140°
Polystyrenes					
MW	30,100	34.00	33.50	32.67	32.22
MW	9,000	39.52	39.05	38.10	37.60
MW	4,000	42.10	43.40	40.87	41.00
MW	2,000	44.37	44.32	43.92	42.35
MW	955	48.47	47.80	-	46.10
MW	570	-	49.30	47.57	46.90
PNA (3 ring or less)					
(206)	9,10-DiMe Anthracene	58.20	57.45	56.42	58.10
(192)	2-Me Phenanthrene	59.67	58.37	58.05	59.60
(178)	Phenanthrene	60.97	60.10	58.75	59.57
(170)	2,3,5-TriMe Naph.	60.95	57.85	58.65	58.30
(166)	Fluorene	60.72	60.10	58.70	58.97
(156)	1,2-DiMe Naph.	60.85	60.22	58.72	58.20
PNA (4 ring or more)					
(300)	Coronene	56.95	56.90	56.37	55.87
(278)	Dibenz[ah]Anthracene	56.87	56.75	55.42	54.65
(276)	Benz[ghi]Per	57.50	57.27	56.15	55.35
(256)	DMBA	56.85	56.55	55.42	54.87
(252)	Perylene	57.82	57.75	56.55	55.85
(228)	Chrysene	58.75	57.80	56.72	56.07
(202)	Pyrene	59.47	58.75	57.95	57.35
N-PNA					
(281)	Dibenz Acridine	71.90	66.67	59.45	58.47
(267)	Dibenz Carbazole	67.42	65.90	60.82	59.57
(179)	Acridine	83.95	75.62	64.47	62.77
(167)	Carbazole	70.17	68.55	64.67	63.07
O-PNA					
(288)	Pyrene butyric acid	ND	ND	85.40	75.72
(284)	Stearic acid	ND	ND	70.90	-
(230)	Pyrene Carboxaldehyde	59.77	59.70	57.80	56.90
(208)	Phen. Quinone	60.95	60.60	58.97	58.45
(206)	Phen. Carboxaldehyde	ND	60.22	58.75	58.20
(194)	Phenanthrol	84.42	79.30	69.52	66.97
(182)	9-Hydroxy fluorene	67.95	66.02	-	60.70
(252)	Anthraquinone-COOH	ND	ND	ND	ND
(226)	Hydroxy fluorene COOH	ND	ND	ND	ND
Saturates					
(891)	Tristearin	47.17	46.87	45.90	45.65
(807)	Tripalmitin	48.42	47.70	46.62	46.17
(395)	n-Octacosane	51.12	50.70	49.50	49.07
(283)	n-Eicosane	53.47	52.92	51.90	51.15
(254)	n-Octadecane	-	53.62	52.47	-
(226)	n-Hexadecane	55.17	54.55	53.65	52.60

ND = none detected - = not determined

TABLE 10

Retention Time Data

Ultrastyragel(10^3+500Å+500Å)/THF/0.5 mL/min @ 35°C

Model Compounds		Retention Time (min)
Polystyrenes		
MW	30,100	29.16
MW	9,000	33.90
MW	4,000	36.40
MW	2,000	38.83
MW	955	41.70
MW	570	43.50
PNA (3 ring or less)		
(206)	9,10-DiMe Anthracene	54.60
(192)	2-Me Phenanthrene	53.20
(178)	Phenanthrene	53.66
(170)	2,3,5-TriMe Naph.	51.73
(166)	Fluorene	52.83
(156)	1,2-DiMe Naph.	52.36
PNA (4 ring or more)		
(300)	Coronene	56.73
(278)	Dibenz[ah]Anthracene	53.06
(276)	Benz[ghi]Per	56.56
(256)	DMBA	54.00
(252)	Perylene	55.80
(228)	Chrysene	53.63
(202)	Pyrene	54.83
N-PNA		
(281)	Dibenz Acridine	52.20
(267)	Dibenz Carbazole	53.70
(179)	Acridine	53.30
(167)	Carbazole	51.70
O-PNA		
(230)	Pyrene Carboxaldehyde	53.80
(208)	Phen. Quinone	50.96
(206)	Phen. Carboxaldehyde	52.43
(194)	Phenanthrol	55.30
(182)	9-Hydroxy Fluorene	50.20
(288)	Pyrene Butyric Acid	60.56
Saturates		
(891)	Tristearin	39.66
(807)	Tripalmitin	40.16
(395)	n-Octacosane	42.73
(283)	n-Eicosane	44.33
(254)	n-Octadecane	44.70
(226)	n-Hexadecane	45.50

WI·SP™ SAMPLE IDENTIFICATION RECORD

Run Identification: TABLE 11

Analysis: Retention Time Data

2 x PSM 60-S/o-Xylene/0.5 mL/min/35°C

Date Dec. 12/13, 1986

Carriage No. _____

Operator _____

Analysis Conditions

Column 2 x PSM 60-S I.D.# DuPont 6.2mm x 25cm

Detector Waters R.I. 410 @ 38°C

Eluent o-Xylene @ 0.5 mL/min @ 35°C
(7.5 mL in 15 min @ 0.5 mL/min setting)

Standards

Detection Sens: 64
Scale Factor : 2
Time Constant : 3

Model Compounds dissolved in o-Xylene (B & J)

System Messages

25 µL Injection
Run Time: 60 min
Eq. Delay: 5 min

No.	Inj. Vol.	No. of Injs.	Ret. Time	Sample Identification	No.	Inj. Vol.	No. of Injs.	Ret. Time	Sample Identification
1			11.76	PS Std. MW 30,100	25			29.46	DiBenz Acridine (281)
2			14.00	PS Std. MW 9,000	26			21.93	DiBenz Carbazole (267)
3			15.53	PS Std. MW 4,000	27			47.83	Acridine (179)
4			16.73	PS Std. MW 2,000	28			21.86	Carbazole (167)
5			18.26	PS Std. MW 955	29			ND	Pyrene Buryric Acid (288)
6			19.10	PS Std. MW 570	30			ND	Anth. Quinone COOH (252)
7			21.70	9,10 DiMeAnthracene(206)	31			ND	Hydroxy Fluorene COOH(22
8			20.70	2-Me Phenanthrene (192)	32			ND	Stearic Acid (284)
9			20.80	Phenanthrene (178)	33			NP	Tristearin (891)
10			20.86	2,3,5-TriMe Naph (170)	34			18.46	Tripalmitin (807)
11			20.86	Fluorene (166)	35			19.40	n-Octacosane (395)
12			20.90	1,2-DiMe Naph (156)	36			20.00	n-Eicosane (283)
13			20.33	Coronene (300)	37			20.16	n-Octadecane (254)
14			20.26	Dibenz[ah]A (278)	38			20.33	n-Hexadecane (226)
15			20.43	Benz[ghi]Per (276)	39				
16			20.40	DMBA (256)	40				
17			20.46	Perylene (252)	41				
18			20.53	Chrysene (228)	42				
19			20.76	Pyrene (202)	43				
20			21.43	Pyrene Carboxaldehyde (230)	44				
21			22.96	Phenanthrene Quinone (208)	45				
22			21.26	Phen. Carboxaldehyde(206)	46				
23			22.86	Phenanthrol (194)	47				
24			24.73	Hydroxy Fluorene (182)	48				

Notes

ND = not detected

NP = not performed

TABLE 12

Retention Time Data

2 x PSM 60-S/o-Xylene/0.3 mL/min/35°C

Model Compounds		Retention Time (min)
Polystyrenes		
MW	30,100	19.68
MW	9,000	21.12
MW	4,000	24.99
MW	2,000	25.82
MW	955	27.83
MW	570	29.54
PNA (3 ring or less)		
(206)	9,10-DiMe Anthracene	
(192)	2-Me Phenanthrene	31.46
(178)	Phenanthrene	31.35
(170)	2,3,5-TriMe Naph.	32.09
(166)	Fluorene	31.66
(156)	1,2-DiMe Naph.	32.24
PNA (4 ring or more)		
(300)	Coronene	30.83
(278)	Dibenz[ah]Anthracene	31.00
(276)	Benz[ghi]Per	30.74
(256)	DMBA	
(252)	Perylene	30.59
(228)	Chrysene	30.51
(202)	Pyrene	31.14
N-PNA		
(281)	Dibenz Acridine	
(267)	Dibenz Carbazole	
(179)	Acridine	
(167)	Carbazole	32.62
O-PNA		
(288)	Pyrene butyric acid	
(284)	Stearic acid	
(230)	Pyrene Carboxaldehyde	
(208)	Phen. Quinone	
(206)	Phen. Carboxaldehyde	
(194)	Phenanthrol	
(182)	9-Hydroxy fluorene	
(252)	Anthraquinone-COOH	
(226)	Hydroxy fluorene COOH	
Saturates		
(891)	Tristearin	
(807)	Tripalmitin	
(395)	n-Octacosane	28.77
(283)	n-Eicosane	29.68
(254)	n-Octadecane	30.04
(226)	n-Hexadecane	30.34

TABLE 13

Retention Time Data

2 x PSM 60-S/o-Xylene/0.3 mL/min/35°C, 60°C and 90°C

	Model Compounds	Retention Time (min)		
		35°C*	60°C*	90°C*
Polystyrenes				
*	MW 30,100	19.00	18.33	18.30
*	MW 9,000	22.76	21.70	21.90
*	MW 4,000	25.16	24.86	24.20
*	MW 2,000	26.93	25.93	26.00
*	MW 955	29.40	28.30	28.20
	MW 570	30.80	29.63	29.33
PNA (3 ring or less)				
	(206) 9,10-DiMe Anthracene	34.86	33.33	32.80
*	(192) 2-Me Phenanthrene	33.10	32.36	31.40
*	(178) Phenanthrene	33.33	31.90	31.43
*	(170) 2,3,5-TriMe Naph.	33.40	32.23	31.56
*	(166) Fluorene	33.43	32.16	31.50
*	(156) 1,2-DiMe Naph.	33.50	32.16	31.56
PNA (4 ring or more)				
*	(300) Coronene	32.76	31.46	30.63
*	(278) Dibenz[ah]Anthracene	32.50	31.13	30.46
*	(276) Benz[ghi]Per	32.53	31.33	30.76
	(256) DMBA	33.83	32.83	32.00
*	(252) Perylene	32.43	31.60	30.90
*	(228) Chrysene	32.90	32.26	31.06
*	(202) Pyrene	33.43	31.93	31.23
N-PNA				
	(281) Dibenz Acridine	47.33	42.56	39.96
	(267) Dibenz Carbazole	35.30	32.83	31.53
	(179) Acridine	74.73	55.83	51.73
*	(167) Carbazole	35.03	32.43	32.23
O-PNA				
	(288) Pyrene butyric acid	50.43	46.03	43.30
	(284) Stearic acid	45.16	41.13	39.13
*	(230) Pyrene Carboxaldehyde	33.43	32.76	32.20
	(208) Phen. Quinone	36.66	35.46	34.73
	(206) Phen. Carboxaldehyde	34.06	32.53	32.06
	(194) Phenanthrol	36.63	35.40	34.70
	(182) 9-Hydroxy fluorene	39.56	36.56	35.03
	(252) Anthraquinone-COOH	ND	55.10	ND
	(226) Hydroxy fluorene COOH	38.83	45.30	34.56
Saturates				
*	(891) Tristearin	29.13	28.10	27.66
*	(807) Tripalmitin	29.60	28.06	28.16
*	(395) n-Octacosane	31.10	29.16	29.50
*	(283) n-Eicosane	32.06	30.16	30.20
*	(254) n-Octadecane	32.33	30.30	30.53
*	(226) n-Hexadecane	32.70	30.83	30.66

* = Model Compounds used for calibration for analysis of heavy crudes at 35°C

ND = none detected

TABLE 14

Retention Time Data

2 x PSM 60-S/TCB/0.1 mL/min/~~35°C, 60°C and 90°C~~

		~~35°C~~	60°C	90°C
Polystyrenes				
MW	30,100	-	38.56	37.13
MW	9,000	49.03	47.20	45.80
MW	4,000	NP	52.60	50.50
MW	2,000	NP	57.40	54.43
MW	955	NP	61.73	60.73
MW	570	NP	64.30	62.46
PNA (3 ring or less)				
(206)	9,10-DiMe Anthracene	NP	67.23	64.73
(192)	2-Me Phenanthrene	69.13	67.90	64.66
(178)	Phenanthrene	69.23	66.46	65.00
(170)	2,3,5-TriMe Naph.	69.96	69.30	67.30
(166)	Fluorene	69.66	68.16	67.40
(156)	1,2-DiMe Naph.	69.76	68.40	67.96
PNA (4 ring or more)				
(300)	Coronene	66.66	64.66	64.60
(278)	Dibenz[ah]Anthracene	67.13	65.43	64.63
(276)	Benz[ghi]Per	67.33	66.23	65.23
(256)	DMBA	ND	ND	64.93
(252)	Perylene	67.43	66.03	65.13
(228)	Chrysene	67.63	67.00	65.60
(202)	Pyrene	68.70	66.03	66.03
N-PNA				
(281)	Dibenz Acridine	ND	ND	ND
(267)	Dibenz Carbazole	71.70	70.83	66.00
(179)	Acridine	ND	ND	ND
(167)	Carbazole	75.23	70.43	68.73
O-PNA				
(288)	Pyrene butyric acid	ND	ND	ND
(284)	Stearic acid	ND	ND	ND
(230)	Pyrene Carboxaldehyde	ND	77.36	71.30
(208)	Phen. Quinone	ND	ND	92.50
(206)	Phen. Carboxaldehyde	ND	ND	ND
(194)	Phenanthrol	ND	ND	92.10
(182)	9-Hydroxy fluorene	ND	ND	94.10
(252)	Anthraquinone-COOH	ND	ND	ND
(226)	Hydroxy fluorene COOH	ND	ND	ND
Saturates				
(891)	Tristearin	NP	NP	NP
(807)	Tripalmitin	66.50	NP	NP
(395)	n-Octacosane	66.50	64.90	63.30
(283)	n-Eicosane	69.73	67.66	67.00
(254)	n-Octadecane	70.33	67.26	67.50
(226)	n-Hexadecane	70.13	68.10	68.80

- = not determined
ND = none detected
NP = not performed

TABLE 15

Retention Time Data

2 x PSM 60-S/Pyridine/0.1 mL/min/35°C

Model Compounds		Retention Time (min)
Polystyrenes		
MW	30,100	39.53
MW	9,000	48.86
MW	4,000	54.06
MW	2,000	58.50
MW	955	63.86
MW	570	66.60
PNA (3 ring or less)		
(206)	9,10-DiMe Anthracene	68.96
(192)	2-Me Phenanthrene	69.00
(178)	Phenanthrene	68.85
(170)	2,3,5-TriMe Naph.	70.66
(166)	Fluorene	69.75
(156)	1,2-DiMe Naph.	70.80
PNA (4 ring or more)		
(300)	Coronene	67.63
(278)	Dibenz[ah]Anthracene	67.23
(276)	Benz[ghi]Per	67.50
(256)	DMBA	68.33
(252)	Perylene	67.33
(228)	Chrysene	67.66
(202)	Pyrene	68.75
N-PNA		
(281)	Dibenz Acridine	67.90
(267)	Dibenz Carbazole	67.50
(179)	Acridine	69.06
(167)	Carbazole	68.16
O-PNA		
(288)	Pyrene butyric acid	71.03
(284)	Stearic acid	72.73
(230)	Pyrene Carboxaldehyde	68.13
(208)	Phen. Quinone	67.60
(206)	Phen. Carboxaldehyde	68.33
(194)	Phenanthrol	67.96
(182)	9-Hydroxy fluorene	68.43
(252)	Anthraquinone-COOH	85.43
(226)	Hydroxy fluorene COOH	69.10
Saturates		
(891)	Tristearin	68.30
(807)	Tripalmitin	68.50
(395)	n-Octacosane	74.76
(283)	n-Eicosane	74.60
(254)	n-Octadecane	75.00
(226)	n-Hexadecane	-

TABLE 16

Retention Time Data

2 x PSM 60-S/THF/0.3 mL/min/35°C

Model Compounds		Retention Time (min)
Polystyrenes		
MW	30,100	17.46
MW	9,000	20.90
MW	4,000	22.86
MW	2,000	24.63
MW	955	26.96
MW	570	28.06
MW	42,800	16.61
PNA (3 ring or less)		
(206)	9,10-DiMe Anthracene	30.06
(192)	2-Me Phenanthrene	30.16
(178)	Phenanthrene	30.17
(170)	2,3,5-TriMe Naph.	30.36
(166)	Fluorene	30.23
(156)	1,2-DiMe Naph.	30.50
PNA (4 ring or more)		
(300)	Coronene	29.50
(278)	Dibenz[ah]Anthracene	29.36
(276)	Benz[ghi]Per	29.63
(256)	DMBA	29.73
(252)	Perylene	29.80
(228)	Chrysene	29.83
(202)	Pyrene	30.00
N-PNA		
(281)	Dibenz Acridine	29.70
(267)	Dibenz Carbazole	29.30
(179)	Acridine	30.73
(167)	Carbazole	29.70
O-PNA		
(288)	Pyrene butyric acid	-
(284)	Stearic acid	-
(230)	Pyrene Carboxaldehyde	29.23
(208)	Phen. Quinone	29.16
(206)	Phen. Carboxaldehyde	29.63
(194)	Phenanthrol	29.53
(182)	9-Hydroxy fluorene	29.60
(252)	Anthraquinone-COOH	-
(226)	Hydroxy fluorene COOH	-
Saturates		
(891)	Tristearin	26.26
(807)	Tripalmitin	26.56
(395)	n-Octacosane	28.50
(283)	n-Eicosane	29.23
(254)	n-Octadecane	29.43
(226)	n-Hexadecane	29.66

TABLE 17

Retention Time Data of Selected Model Compounds

Ultrastyragel (10^3+500Å+500Å)/0.5 mL/min

o-Xylene (35°C, 90°C), TCB (90°C, 140°C) and THF (35°C)

Model Compound	Retention Time in Styragel/ THF 35°C @ 0.5 mL/min (min)	Retention Time in Styragel/ o-Xylene 35°C @ 0.5 mL/min (min)	Retention Time in Styragel/ o-Xylene 90°C @ 0.5 mL/min (min)	Retention Time in Styragel/ TCB 90°C @ 0.5 mL/min (min)	Retention Time in Styragel/ TCB 140°C @ 0.5 mL/min (min)
PS 955	41.70	41.82	40.40	47.80	46.10
PS 570	43.50	43.95	42.42	49.30	46.90
2-Me Phen.(192)	53.20	53.50	51.07	58.37	59.60
Phenanthrene (178)	53.66	54.50	52.12	60.10	59.57
TriMe Naph (170)	51.73	51.97	49.95	57.85	58.30
Fluorene (166)	52.83	53.52	51.42	60.10	58.97
DiMe Naph (156)	52.36	52.60	50.52	60.22	58.20
Coronene (300)	56.73	55.42	52.80	56.90	55.87
Benz[ghi]Per (276)	56.56	55.72	52.81	57.27	55.35
Perylene (252)	55.80	55.50	52.77	57.75	55.85
Chrysene (228)	53.63	54.30	51.87	57.80	56.07
Pyrene (202)	54.83	55.05	52.60	58.75	57.35
Dibenz Acr. (281)	52.20	63.12	55.87	66.67	58.47
Dibenz Carz. (267)	53.70	65.65	58.02	65.90	59.57
Acridine (179)	53.30	68.75	59.07	- (> 75 min)	62.77
Carbazole (167)	51.70	60.32	56.50	68.55	63.07
Pyrene Carboxaldehyde (230)	53.80	55.42	53.17	59.70	56.90
Phen. Quinone (208)	50.96	55.25	53.47	60.60	58.45
Phenanthrol (194)	55.30	- (> 73 min)	62.50	- (> 79 min	66.97
Hydroxy Fluorene (182)	50.20	59.27	55.07	66.02	60.70
Tristearin (891)	39.66	39.90	38.67	46.87	45.65
Tripalmitin (807)	40.16	40.52	39.30	47.70	46.17
n-Octacosane (395)	42.73	42.82	41.47	50.70	49.07
n-Eicosane (283)	42.33	44.55	43.17	52.92	51.15
n-Octadecane (254)	44.70	45.20	43.72	53.62	-
n-Hexadecane (226)	45.50	45.77	44.27	54.55	52.60

TABLE 18

Retention Time Data of Selected Model Compounds

PSM 60-S/0.5 mL/min, o-Xylene (35°C) (From Data in Table 11)

Model Compound	Retention Time in PSM 60-S/o-Xylene/ 35°C @ 0.5 mL/min (min)
PS 955	18.26
PS 570	19.10
2-Me Phen.(192)	20.70
Phenanthrene (178)	20.80
TriMe Naph (170)	20.86
Fluorene (166)	20.86
DiMe Naph (156)	20.90
Coronene (300)	20.33
Benz[ghi]Per (276)	20.43
Perylene (252)	20.46
Chrysene (228)	20.53
Pyrene (202)	20.76
Dibenz Acr. (281)	29.46
Dibenz Carz. (267)	21.93
Acridine (179)	47.83
Carbazole (167)	21.86
Pyrene Carboxaldehyde (230)	21.43
Phen. Quinone (208)	22.96
Phenanthrol (194)	22.86
Hydroxy Fluorene (182)	24.73
Tristearin (891)	-
Tripalmitin (807)	18.46
n-Octacosane (395)	19.40
n-Eicosane (283)	20.00
n-Octadecane (254)	20.16
n-Hexadecane (226)	20.33

TABLE 19

Retention Time Data of Selected Model Compounds

PSM 60-S/0.3 mL/min, o-Xylene (35°C and 90°C), THF (35°C)
(From Data in Tables 13 and 16)

Model Compound	Retention Time in PSM 60-S/o-Xylene/ 35°C @ 0.3 mL/min (min)	Retention Time in PSM 60-S/o-Xylene 90°C @ 0.3 mL/min (min)	Retention Time PSM 60-S/THF/ 35°C @ 0.3 mL/min (min)
PS 955	29.40	28.20	26.96
PS 570	30.80	29.33	28.06
2-Me Phen.(192)	33.10	31.40	30.16
Phenanthrene (178)	33.33	31.43	30.17
TriMe Naph (170)	33.40	31.56	30.36
Fluorene (166)	33.43	31.50	30.23
DiMe Naph (156)	33.50	31.56	30.50
Coronene (300)	32.76	30.63	29.50
Benz[ghi]Per (276)	32.53	30.76	29.63
Perylene (252)	32.43	30.90	29.80
Chrysene (228)	32.90	31.06	29.83
Pyrene (202)	33.43	31.23	30.00
Dibenz Acr. (281)	47.33	39.96	29.70
Dibenz Carz. (267)	35.30	31.53	29.30
Acridine (179)	> (74 min)	51.73	30.73
Carbazole (167)	35.03	32.23	29.70
Pyrene Carboxaldehyde (230)	33.43	32.20	29.23
Phen. Quinone (208)	36.66	34.73	29.16
Phenanthrol (194)	36.63	34.70	29.53
Hydroxy Fluorene (182)	39.56	35.03	29.60
Tristearin (891)	29.13	27.66	26.26
Tripalmitin (807)	29.60	28.16	26.56
n-Octacosane (395)	31.10	29.50	28.50
n-Eicosane (283)	32.06	30.20	29.23
n-Octadecane (254)	32.33	30.53	29.43
n-Hexadecane (226)	32.70	30.66	29.66

TABLE 20

Retention Time Data of Selected Model Compounds

PSM 60-S/0.1 mL/min, TCB (90°C) and Pyridine (35°C)

(From Data in Tables 14 and 15)

Model Compound	Retention Time in PSM 60-S/TCB 90°C @ 0.1 mL/min (min)	Retention Time in PSM 60-S/Pyridine 35°C @ 0.1 mL/min (min)
PS 955	60.73	63.86
PS 570	62.46	66.60
2-Me Phen.(192)	64.66	69.00
Phenanthrene (178)	65.00	68.86
TriMe Naph (170)	67.30	70.66
Fluorene (166)	67.40	69.76
DiMe Naph (156)	67.96	70.80
Coronene (300)	64.60	67.63
Benz[ghi]Per (276)	65.23	67.50
Perylene (252)	65.13	67.33
Chrysene (228)	65.60	67.66
Pyrene (202)	66.03	68.75
Dibenz Acr. (281)	ND*	67.90
Dibenz Carz. (267)	66.00	67.50
Acridine (179)	ND	69.06
Carbazole (167)	68.73	68.16
Pyrene Carboxaldehyde (230)	71.30	68.13
Phen. Quinone (208)	92.50	67.60
Phenanthrol (194)	92.10	67.96
Hydroxy Fluorene (182)	94.10	68.43
n-Octacosane (395)	63.30	74.76
n-Eicosane (283)	67.00	74.60
n-Octadecane (254)	67.50	75.00
n-Hexadecane (226)	68.80	-

* ND = none detected

TABLE 21

Molar Volumes (Literature Values) of 8 PNA and 4 Saturates Model Compounds and their Retention Times in Ultrastyragel (1000Å+500Å+500Å)/35°C/0.5 mL/min in o-Xylene and in THF; and in 2 x PSM 60-S/35°C/0.3 mL/min in o-Xylene and THF Systems

Model Compound	Molecular Weight	Molar Volume (Cm^3/g mole)	Retention Time in Ultrastyragel/ o-Xylene/ 35°C @ 0.5 mL/min (min)	Retention Time in PSM 60-S/ o-Xylene/ 35°C @ 0.3 mL/min (min)	Retention Time in Ultrastyragel/ THF/ 35°C @ 0.5 mL/min (min)	Retention Time in PSM 60-S/ THF/ 35°C @ 0.3 mL/min (min)
PAH's						
Coronene	300	228.2	55.42	30.83	56.73	29.50
Benz[ghi]Per	276	219.0	55.72	30.74	56.56	29.63
Perylene	252	202.0	55.50	30.59	55.80	29.80
Chrysene	228	193.8	54.30	30.51	53.63	29.83
Pyrene	202	171.5	55.05	31.14	54.83	30.00
Phenanthrene	178	158.8	54.50	31.35	53.66	30.17
Fluorene	166	153.2	53.52	31.66	52.83	30.23
Carbazole	167	144.3	60.32	32.62	51.70	29.70
Saturates						
n-Octacosane	395	503	42.82	28.77	42.73	28.50
n-Eicosane	283	382	44.55	29.68	44.33	29.23
n-Octadecane	254	350	45.20	30.04	44.70	29.43
n-Hexadecane	226	311	45.77	30.34	45.50	29.66

TABLE 22

MW and MWD Results of Analysis of Heavy Crude Samples

in 2 x PSM 60-S/o-Xylene/35°C/0.3 mL/min

Sample	Mw	Mn	Mw/Mn	Calibration	SEC Profile
Lloydminster Heavy Oil	1791	425	4.209	Figure 18	Figure 20
Cold Lake Heavy Oil	2412	637	3.785	Figure 18	Figure 21
Visbreaking Residue	1200	631	1.901	Figure 19	Figure 22
Visbreaking C_7 Asphaltene	1726	651	2.650	Figure 19	Figure 23
Lloydminster C_7 Asphaltene	6423	1108	5.796	Figure 19	Figure 24

TABLE 23

MW and MWD of Heavy Crude Samples

SEC Molecular Weights of Heavy Oil Asphaltene Samples

(SEC Conditions: 2 x PSM 60-S columns;

THF @ 0.3 mL/min @ 35°C)

Sample	Mw	Mn	Mw/Mn	Calibration	SEC Profile
Lloydminster Heavy Oil	2113	503	4.200	Fig. 25 (linear)	-
Lloydminster Heavy Oil	2148	510	4.211	Fig. 25 (cubic)	-
Cold Lake Heavy Oil	2484	614	4.045	Fig. 25 (linear)	-
Cold Lake Heavy Oil	2497	625	3.992	Fig. 25 (cubic)	Figure 28
Lloydminster Heavy Oil	2118	519	4.080	Fig. 26 (cubic)	-
Lloydminster Heavy Oil	2014	507	3.972	Fig. 27 (linear)	-
Lloydminster Heavy Oil	1998	497	4.019	Fig. 27 (cubic)	Figure 29
Visbreaking Residue	1054	604	1.734	Fig. 27 (cubic)	Figure 30
Visbreaking C_7 Asphaltene	1728	684	2.524	Fig. 27 (cubic)	Figure 31
Lloydminster C_7 Asphaltene	8488	1700	4.990	Fig. 27 (cubic)	Figure 32

TABLE 24

Results of Number Average Molecular Weight

and Intrinsic Viscosity of Heavy Crude Samples and Standards

Sample	Molecular Weight			Intrinsic Viscosity $\times 10^{-3}$ (g/g)*
	Freezing Point Depression	Vapour Pressure Osmometry		temp. = 25.4°C
	Cyclohexanone	Benzene	o-Xylene	o-Xylene
Lloydminster Heavy Oil	817.9	793	764	0.0036
Visbreaking Residue		880	920	0.0036
Cold Lake Heavy Oil	786.3	769	792	0.0073
Lloydminster C_7 Asphaltene		7,949	*	
Visbreaking C_7 Asphaltene		3,270	2,903	
Pyrene (202.3)			218	
n-Octacosane (394.8)			432	

* g of Solute per g of solvent

(can be converted to cc g^{-1})

FIGURES 1 - 37

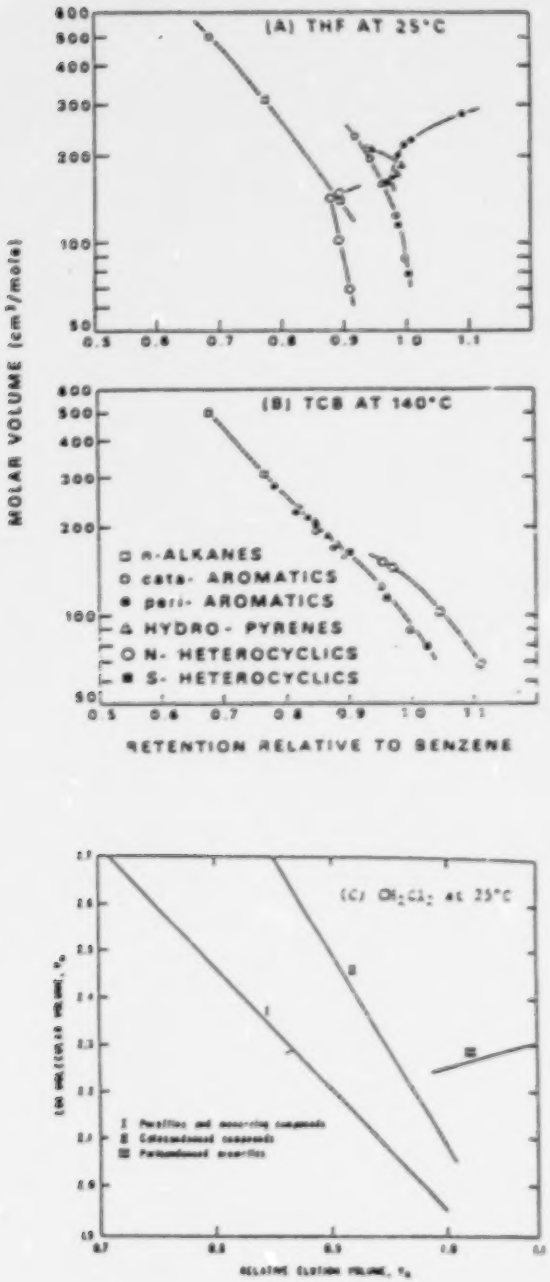


FIGURE 1

Effect of Solvent on Elution Behaviour
of Model Compounds in SEC on Polystyrene Gel

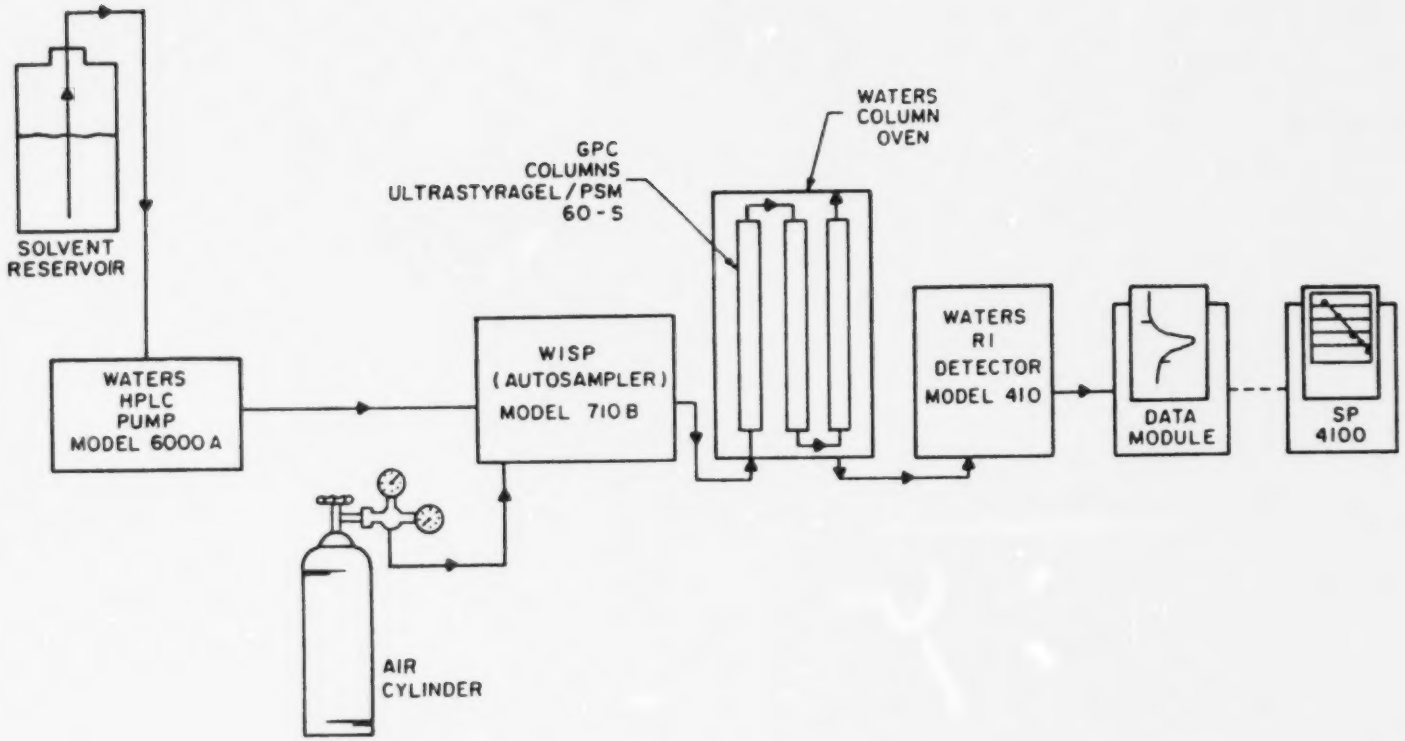


FIGURE 2

Apparatus used for SEC Experiments
and Analysis of Heavy Crude Samples

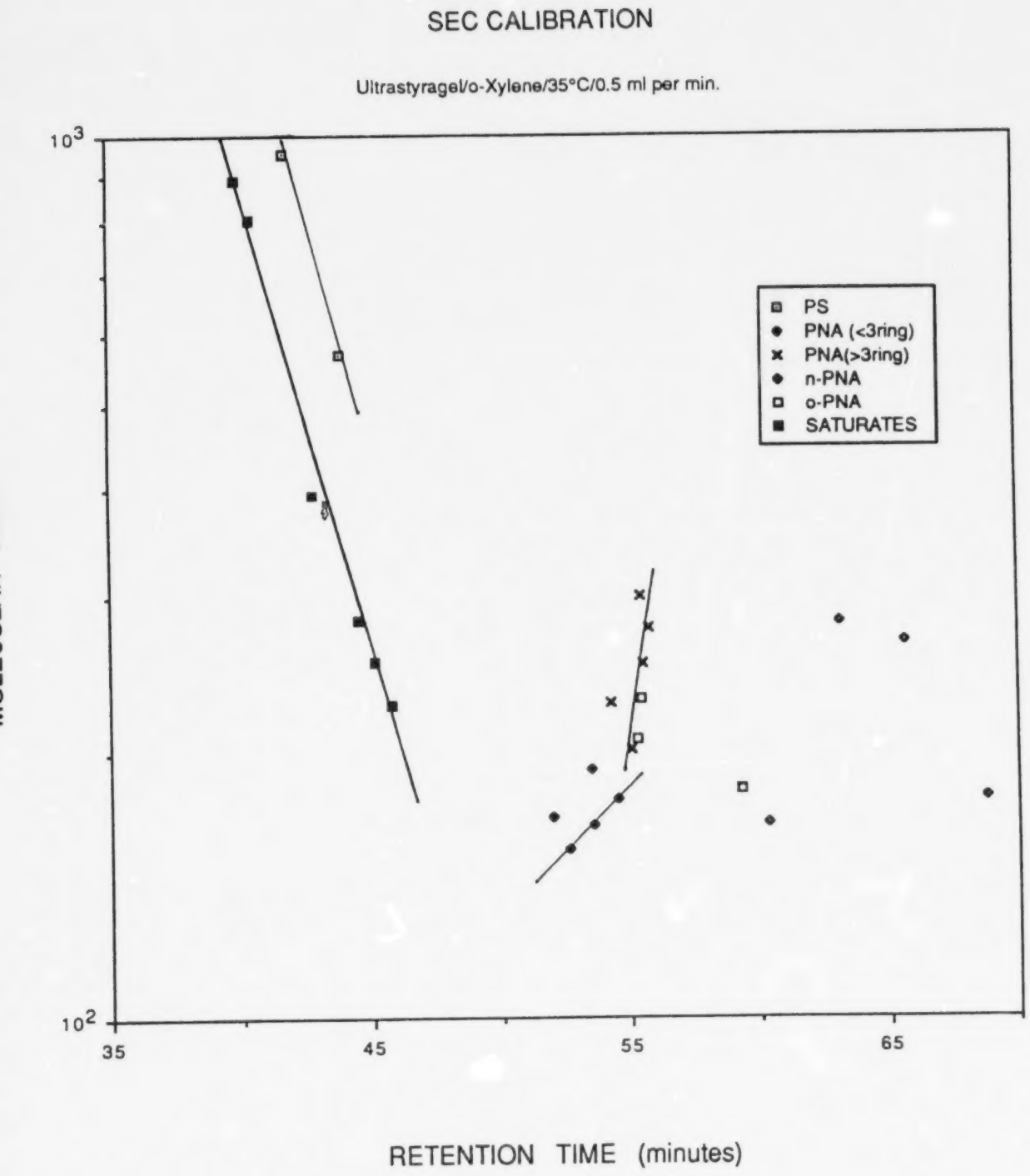


FIGURE 3

Calibration Plots/Curves of 26 Selected Model Compounds
Ultrastyragel (10^3+500Å+500Å)/o-Xylene/35°C
0.5 mL/min (Data in Table 17)

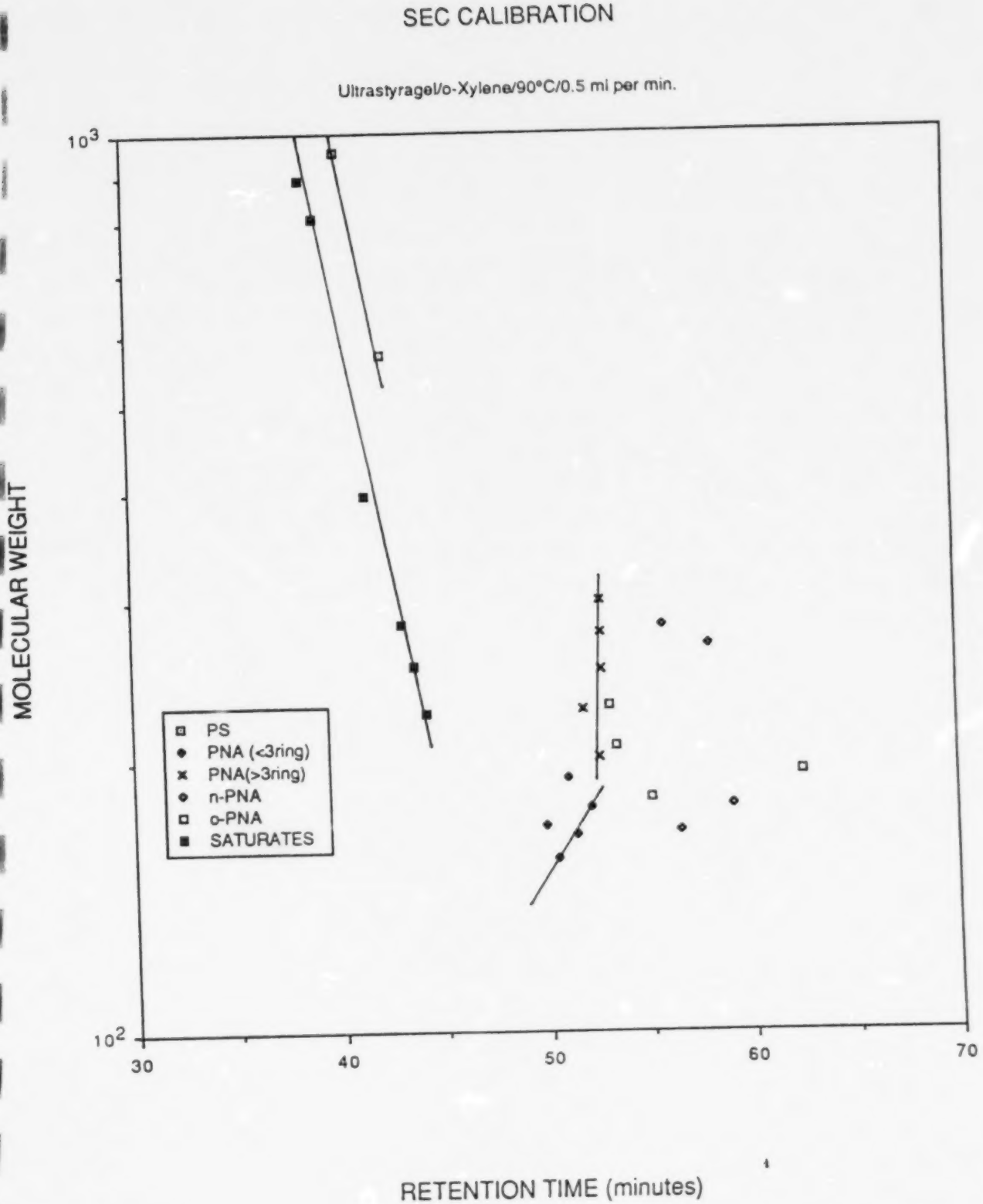


FIGURE 4

Calibration Plots/Curves of 26 Selected Model Compounds
Ultrastyragel (10^3+500Å+500Å)/o-Xylene/90°C
0.5 mL/min (Data in Table 17)

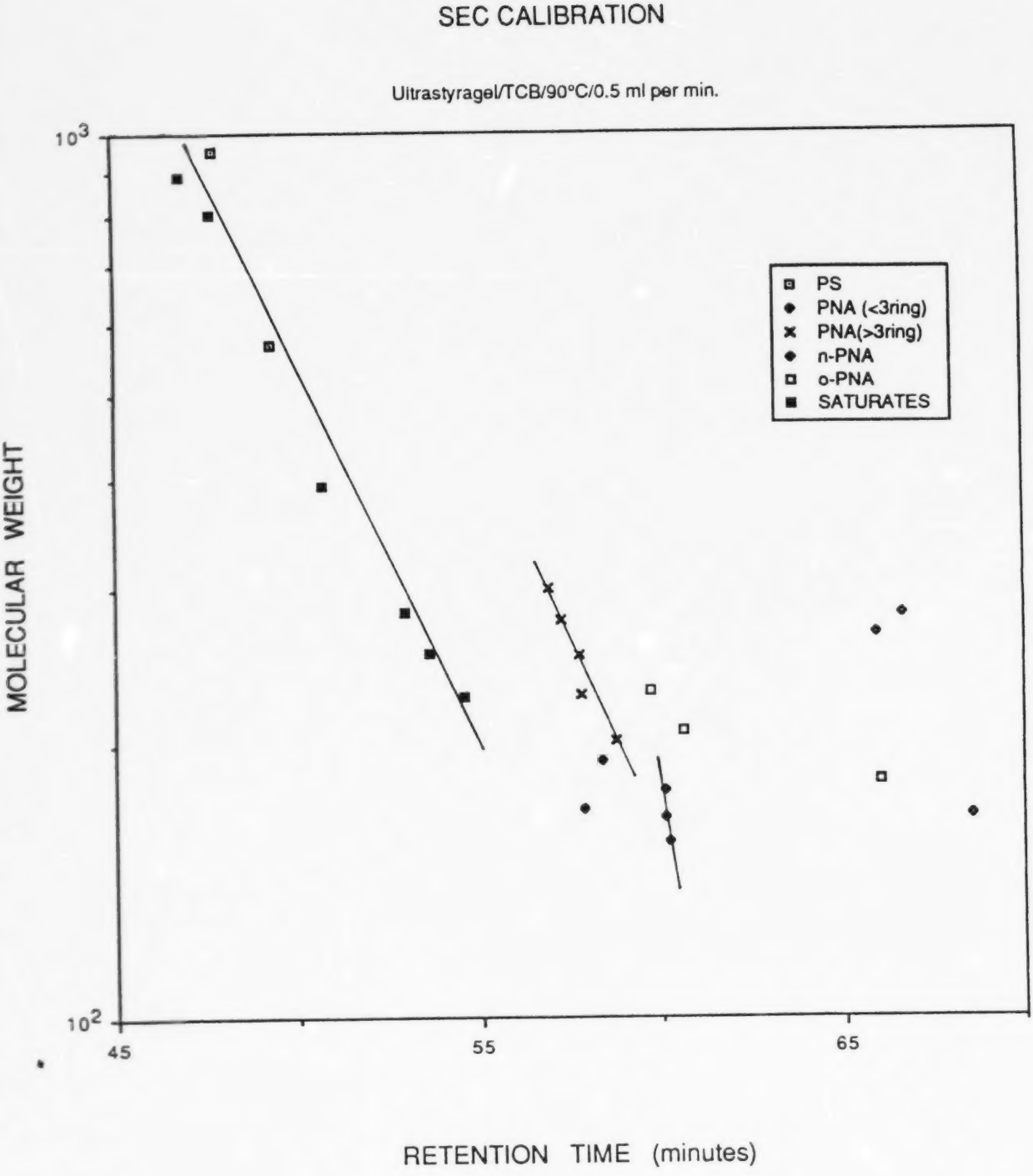


FIGURE 5

Calibration Plots/Curves of 26 Selected Model Compounds
Ultrastyragel (10^3+500Å+500Å)/TCB/90°C
0.5 mL/min (Data in Table 17)

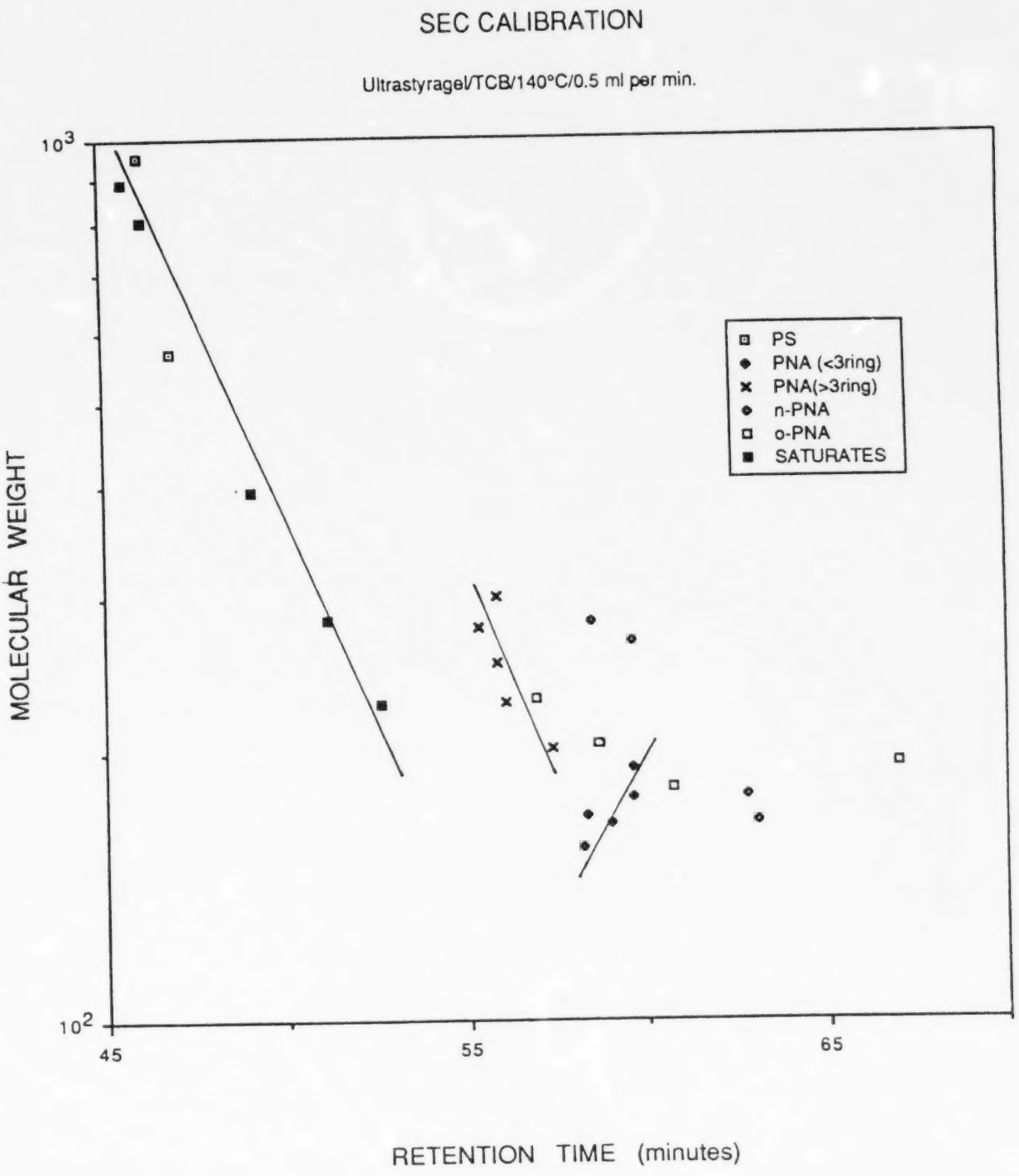


FIGURE 6

Calibration Plots/Curves of 26 Selected Model Compounds
Ultrastyragel (10^3+500Å+500Å)/TCB/140°C
0.5 mL/min (Data in Table 17)

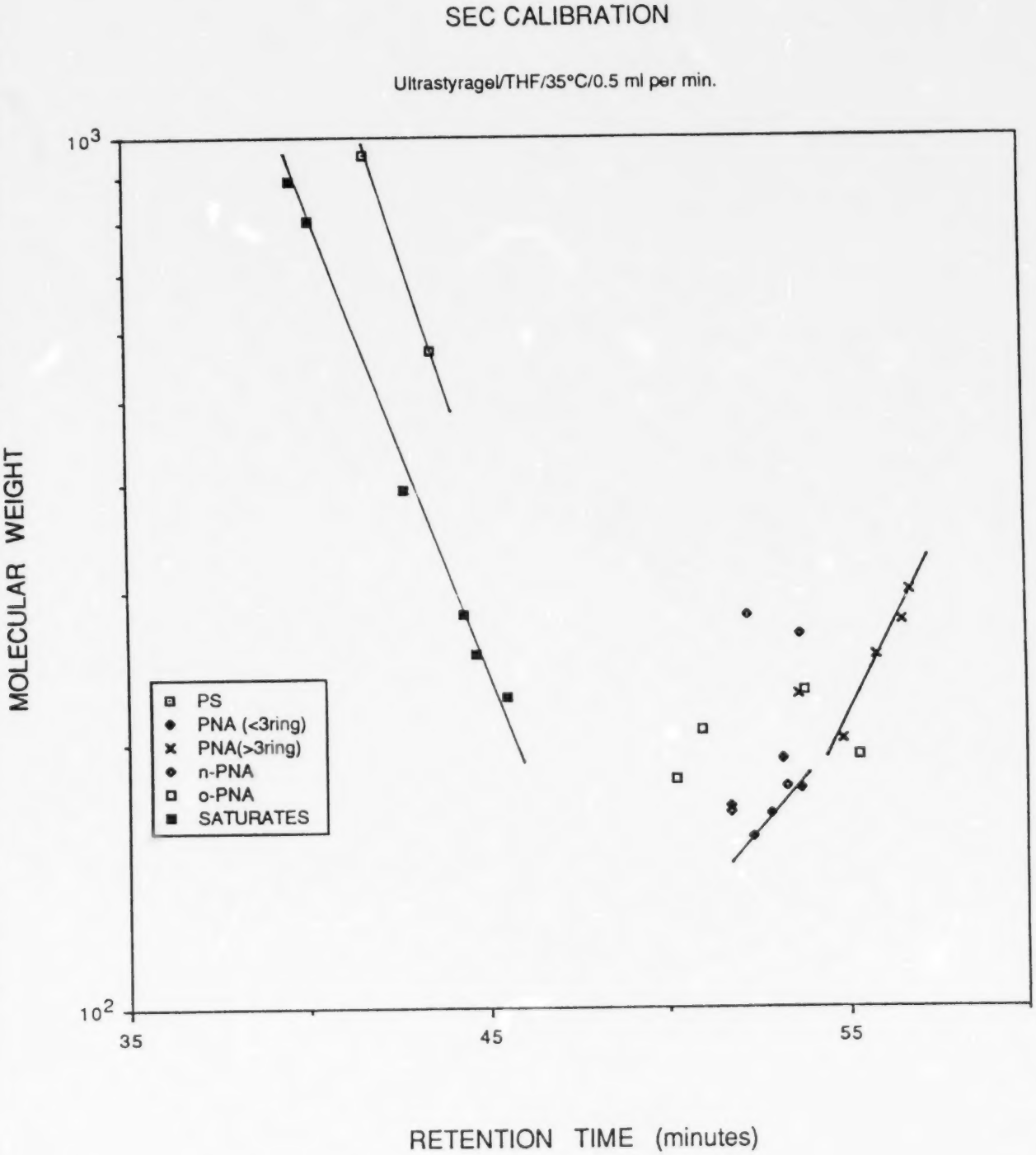


FIGURE 7

Calibration Plots/Curves of 26 Selected Model Compounds
Ultrastyragel (10^3+500Å+500Å)/THF/35°C
0.5 mL/min (Data in Table 17)

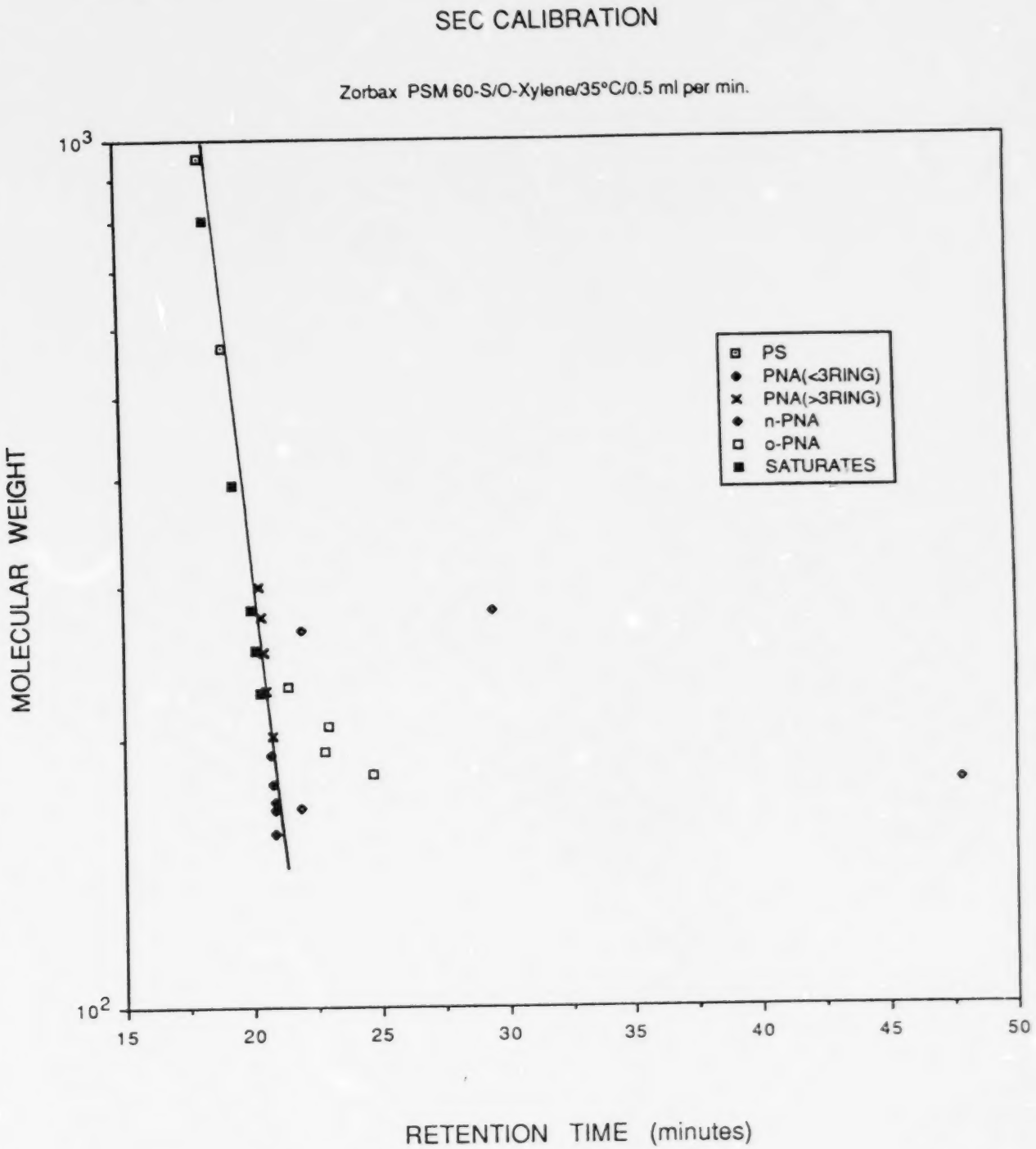


FIGURE 8

Calibration Plots/Curves of 26 Selected Model Compounds
2 x PSM 60-S/o-Xylene/35°C/0.5 mL/min
(Data in Table 18)

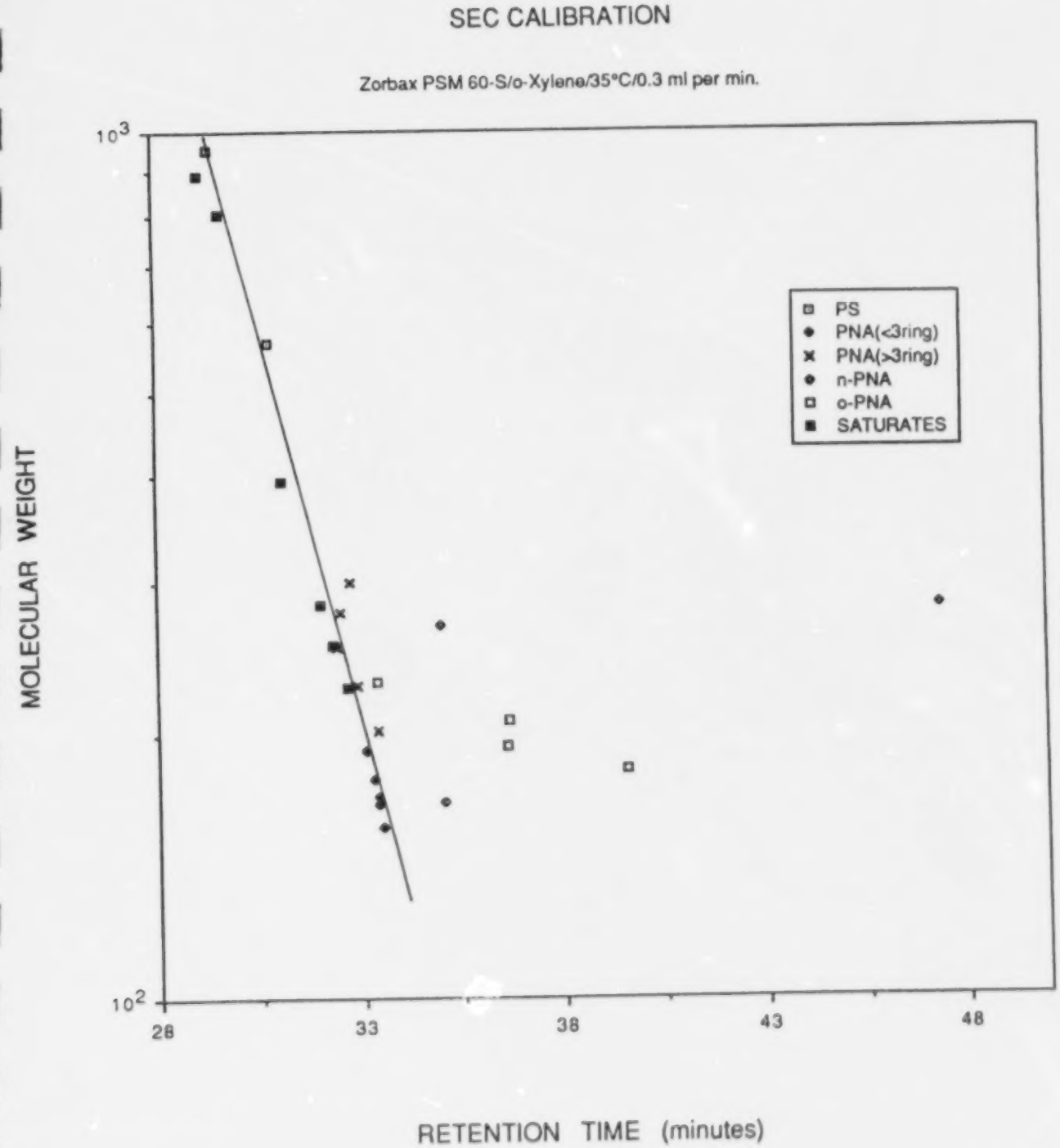


FIGURE 9

Calibration Plots/Curves of 26 Selected Model Compounds
2 x PSM 60-S/o-Xylene/35°C/0.3 mL/min
(Data in Table 19)

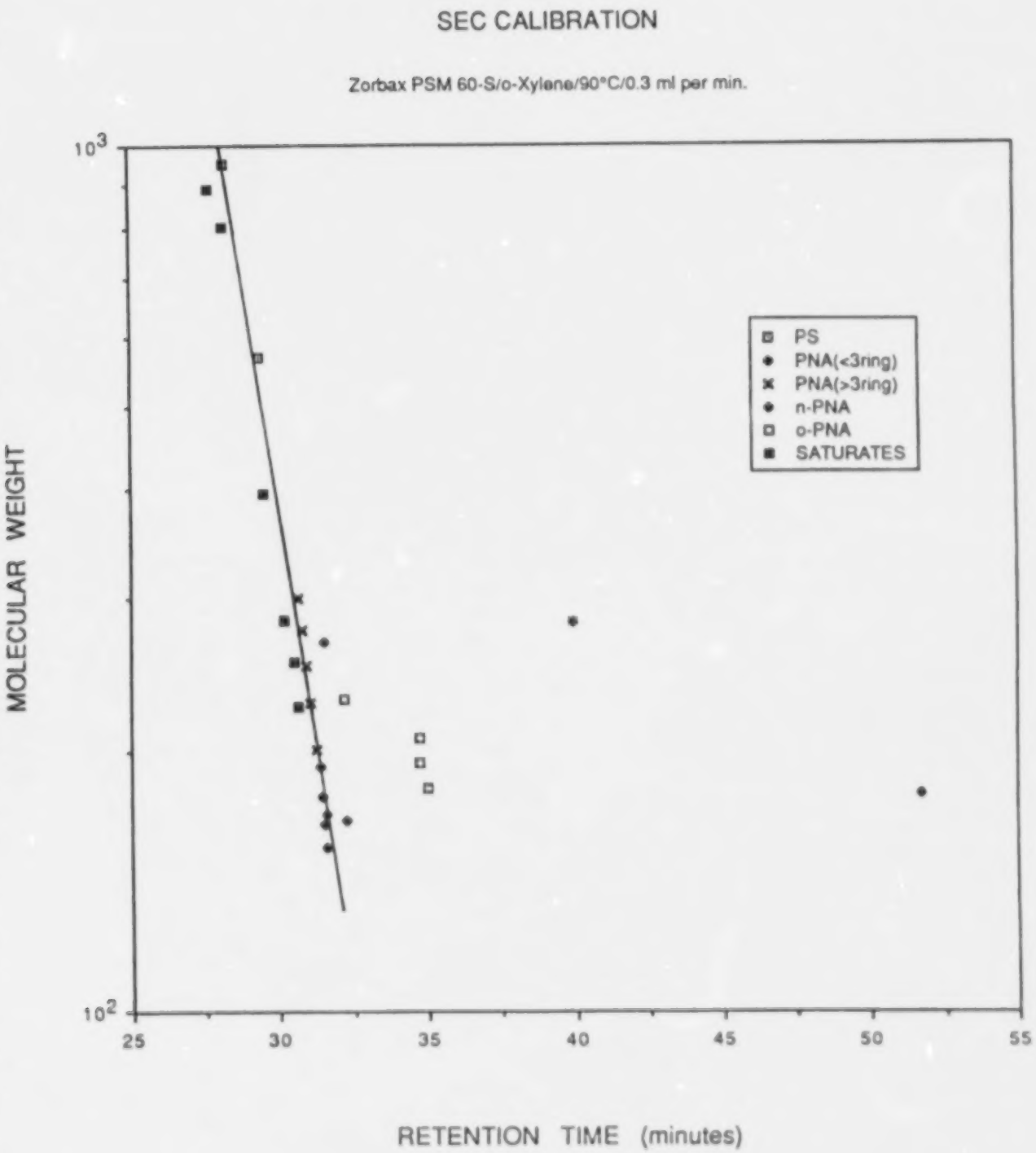


FIGURE 10

Calibration Plots/Curves of 26 Selected Model Compounds
2 x PSM 60-S/o-Xylene/90°C/0.3 mL/min
(Data in Table 19)

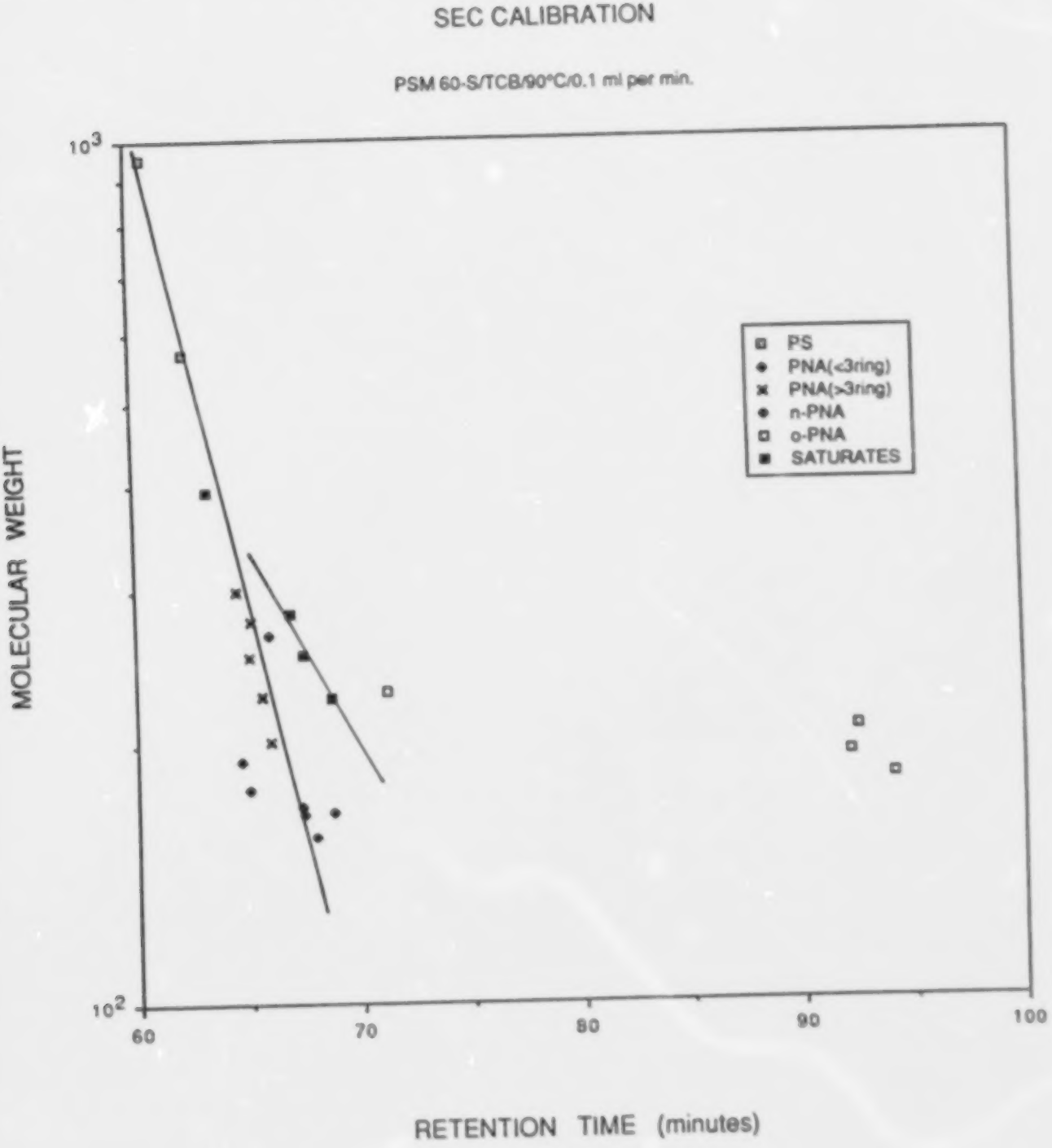


FIGURE 11

Calibration Plots/Curves of 26 Selected Model Compounds
2 x PSM 60-S/TCB/90°C/0.1 mL/min
(Data in Table 20)

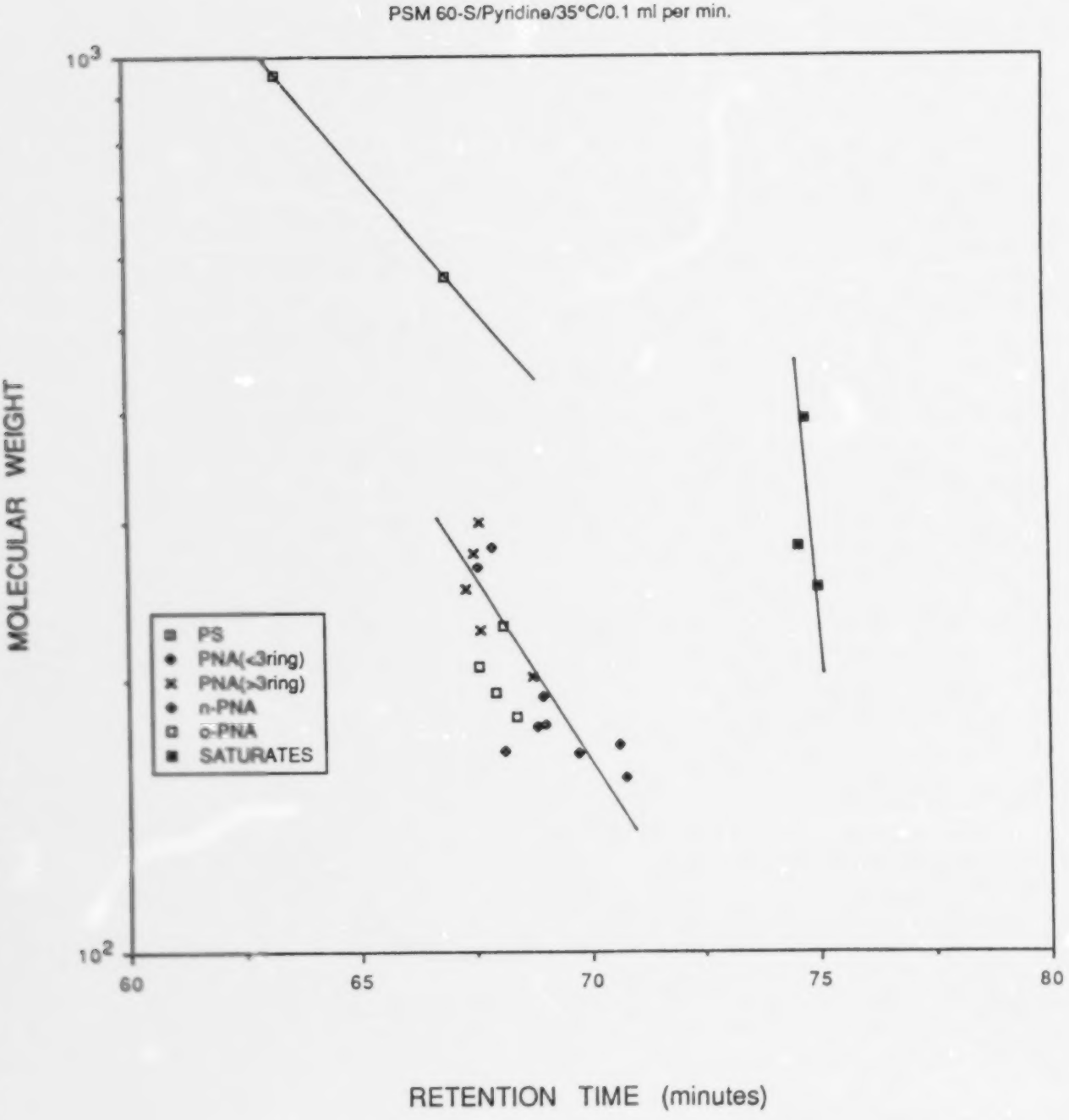


FIGURE 12

Calibration Plots/Curves of 26 Selected Model Compounds
2 x PSM 60-S/Pyridine/35°C/0.1 mL/min
(Data in Table 20)

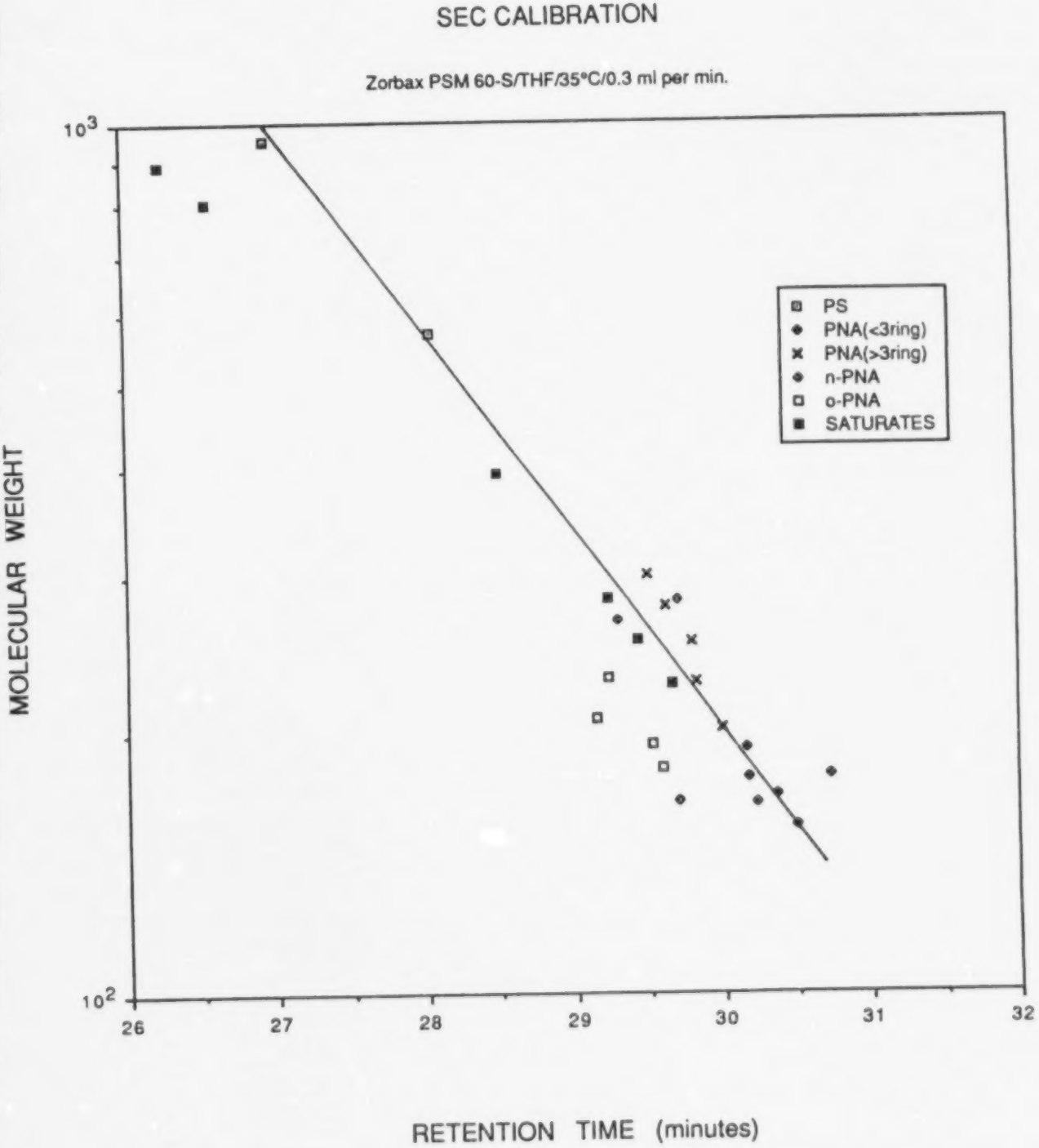
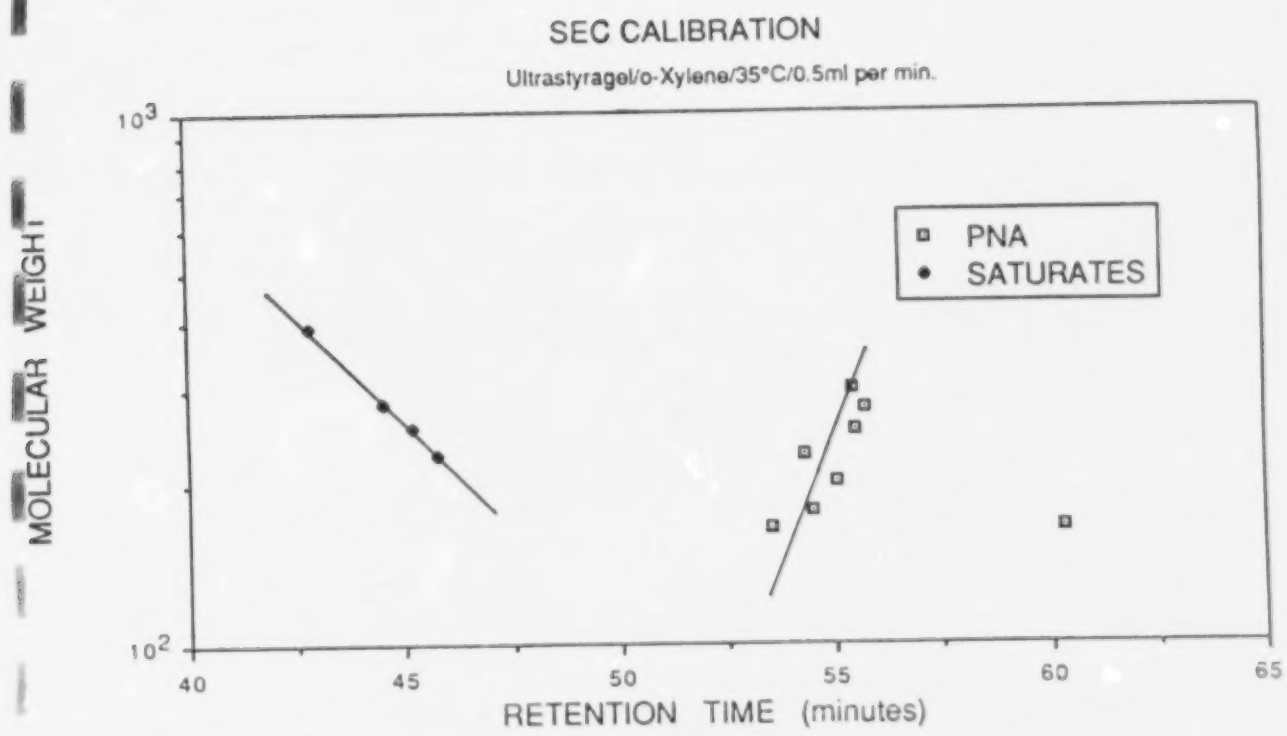


FIGURE 13

Calibration Plots/Curves of 26 Selected Model Compounds
2 x PSM 60-S/THF/35°C/0.3 mL/min
(Data in Table 19)



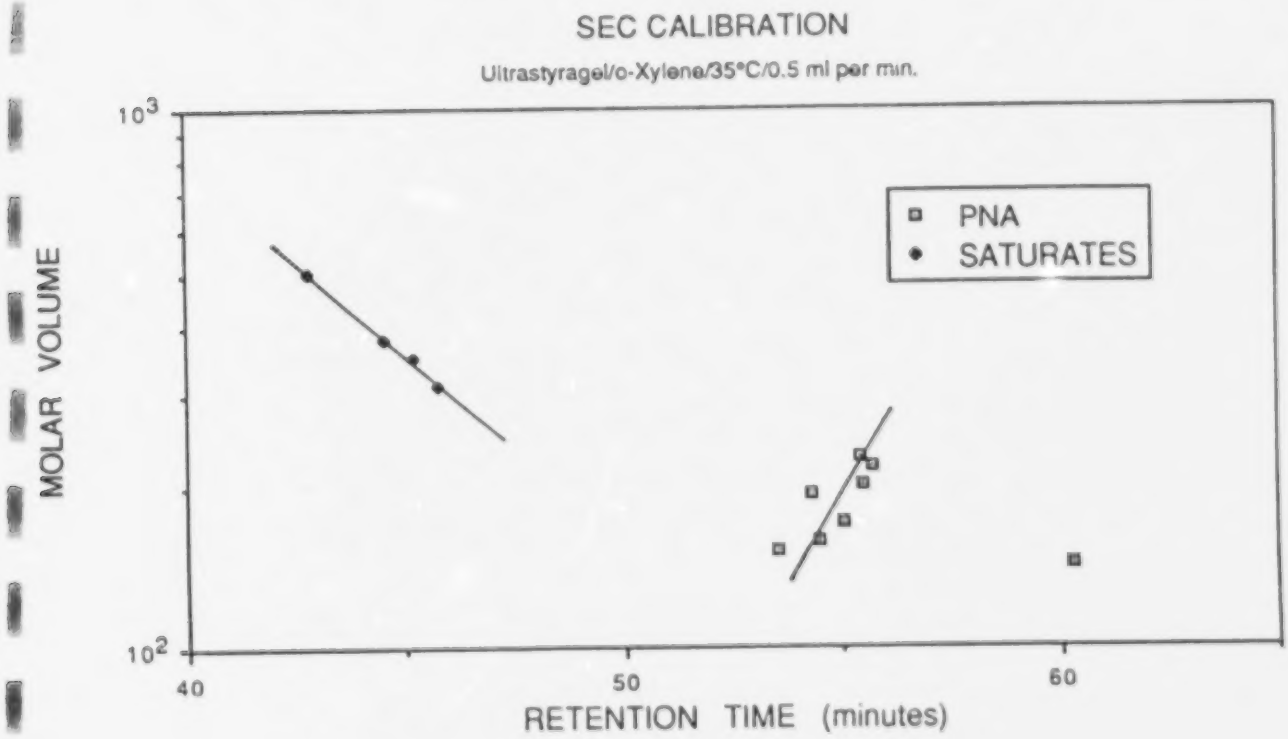
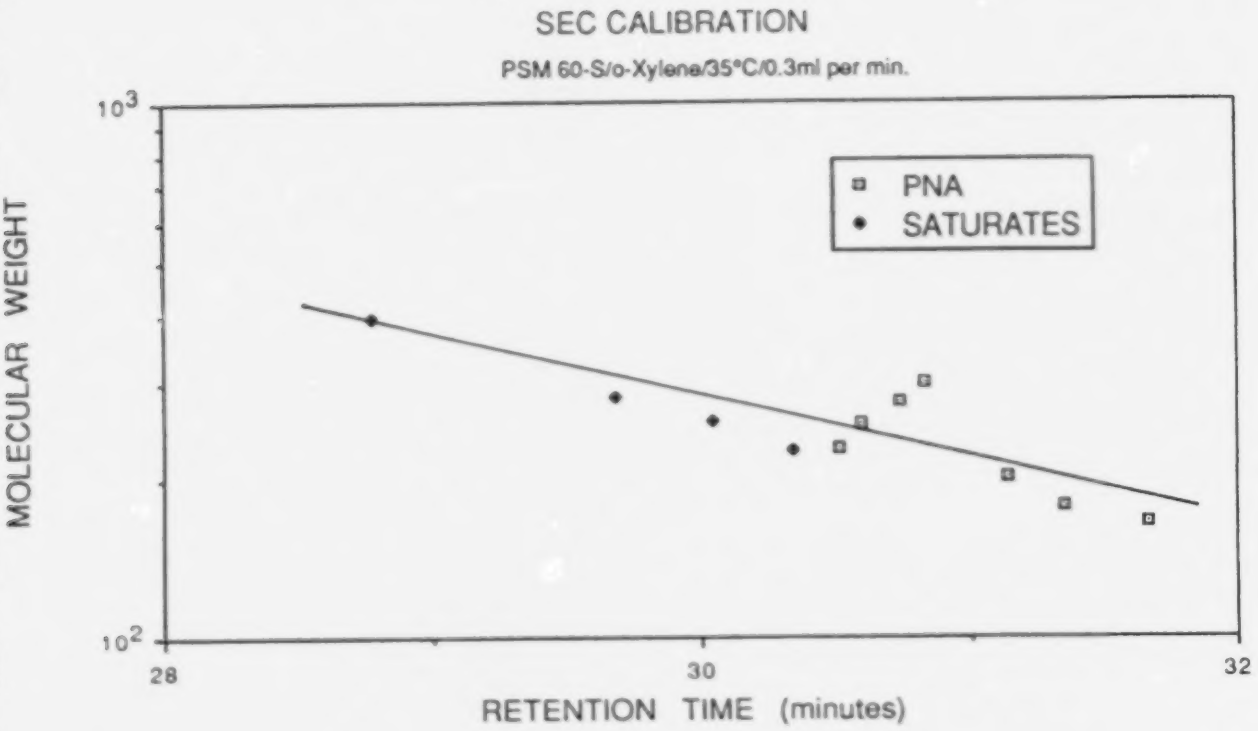


FIGURE 14

Molar Volume/Retention Time and MW/Retention Time Calibration Plots/Curves of 8 PNA and 4 Saturates in Ultrastyragel (1000Å+500Å+500Å)/o-Xylene/ 35°C/0.5 mL/min (Data in Table 21)



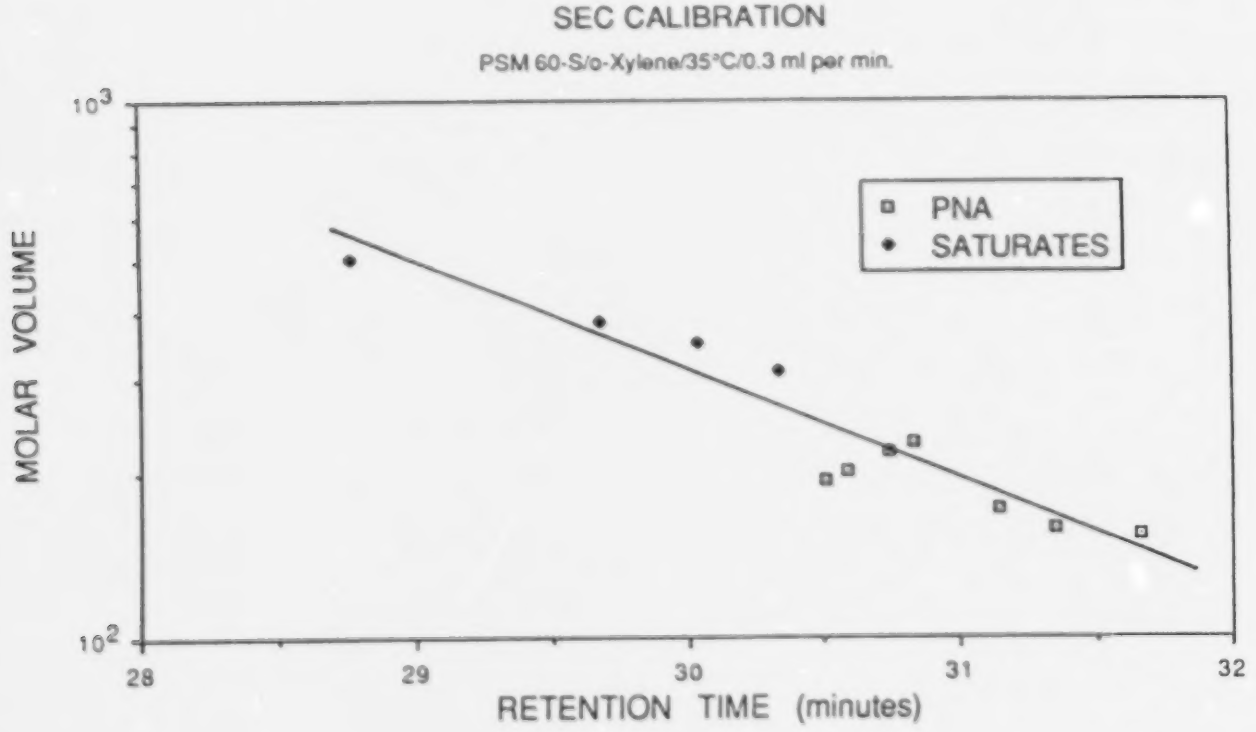
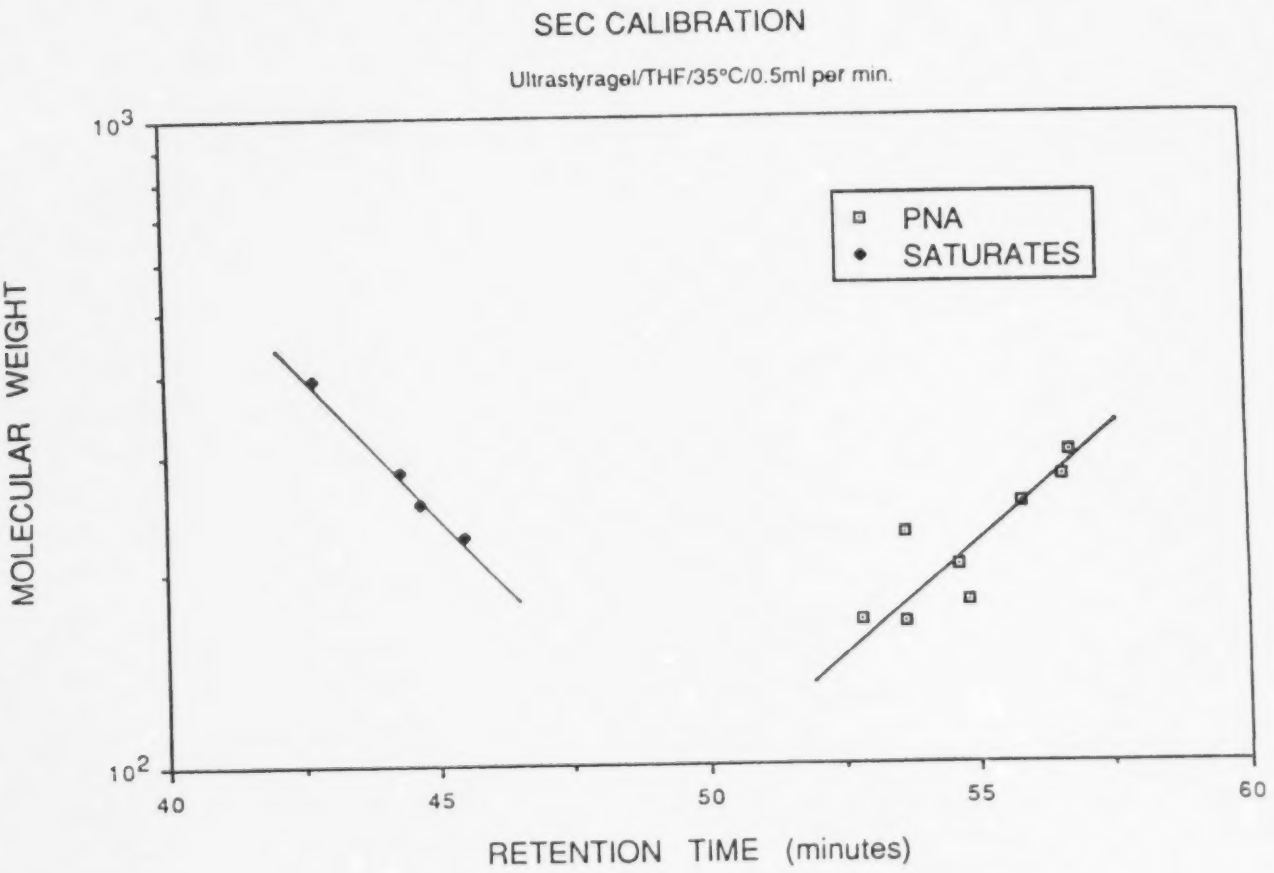


FIGURE 15

Molar Volume/Retention Time and MW/Retention Time
Calibration Plots/Curves of 8 PNA and 4 Saturates
in 2 x PSM 60-S/o-Xylene/35°C/0.3 mL/min
(Data in Table 21)



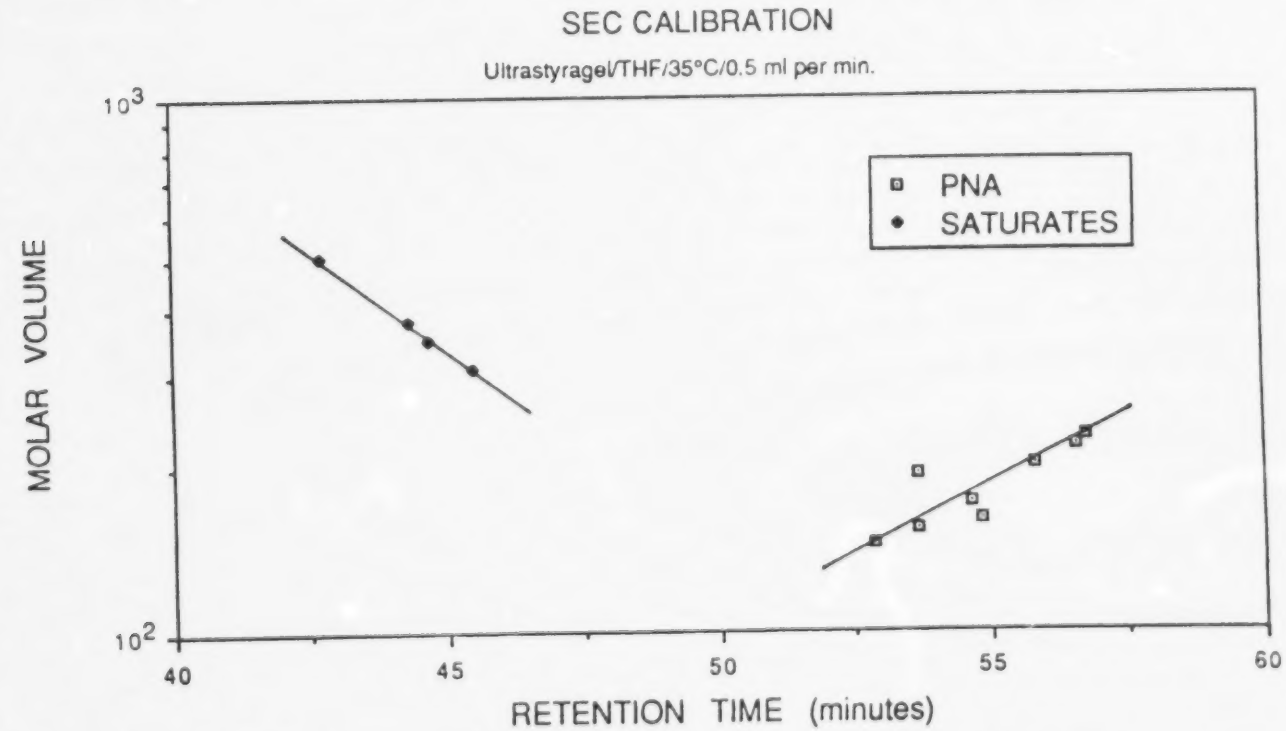
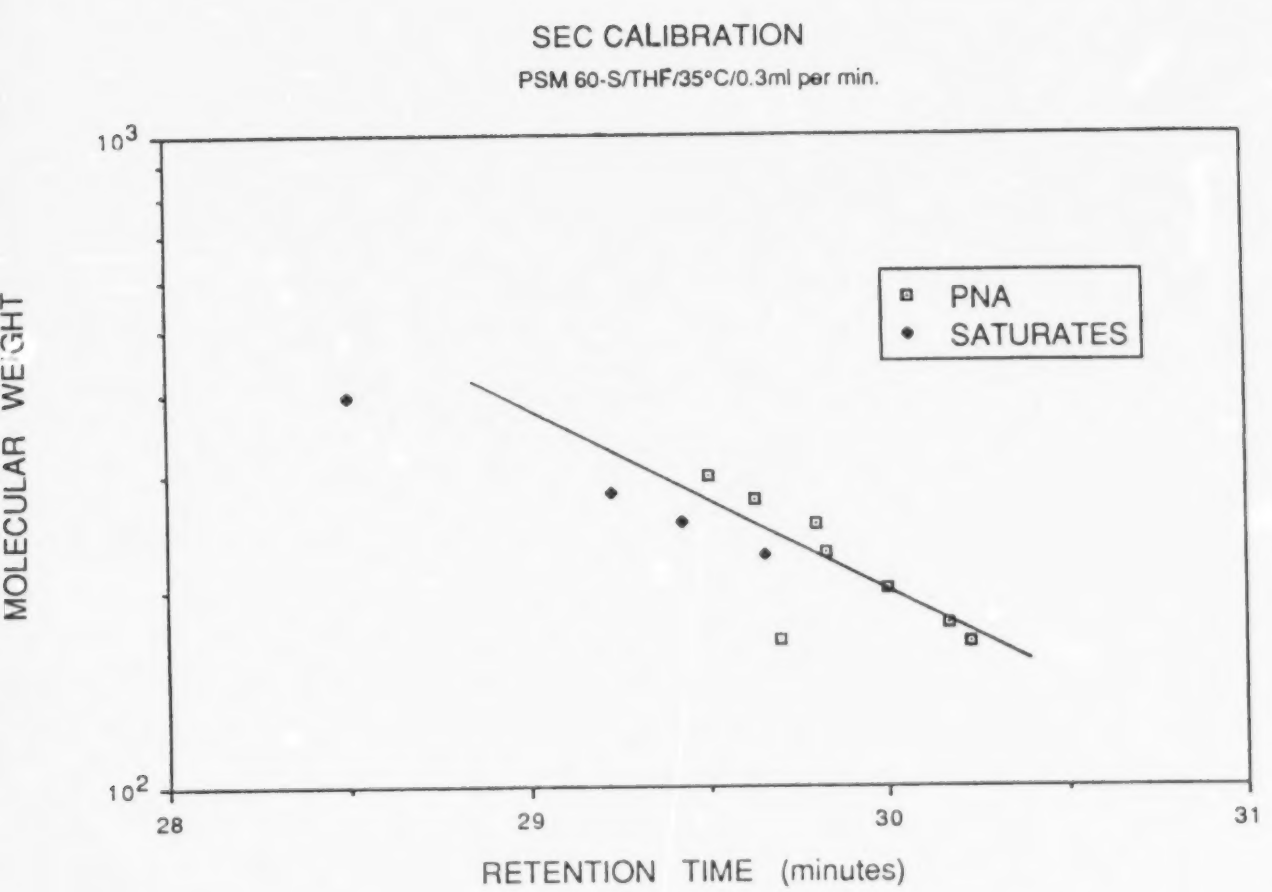


FIGURE 16 Molar Volume/Retention Time and MW/Retention Time Calibration Plots/Curves of 8 PNA and 4 Saturates in Ultrastyragel (1000Å+500Å+500Å)/THF/ 35°C/0.5 mL/min (Data in Table 21)



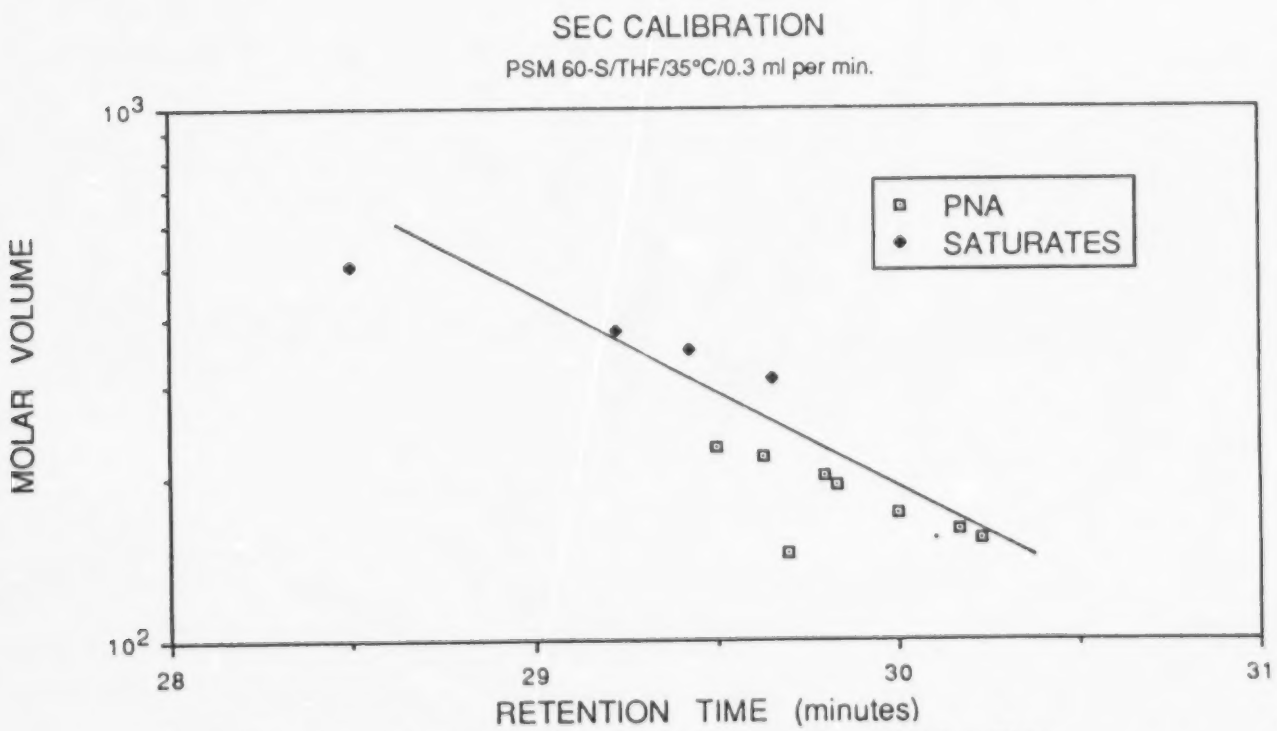


FIGURE 17 Molar Volume/Retention Time and MW/Retention Time Calibration Plots/Curves of 8 PNA and 4 Saturates 2 x PSM 60-S/THF/35°C/0.3 mL/min (Data in Table 21)

```
  READY
BAUD12M0
LIST
      ERROR    3
LOAD"CAL"
TEST
      ERROR   16
GPC Calibration File  1.
Press 'ENTER' to skip entry
Ref Rel Time(RP):
Area Slice Width (mins)(Ta): .5
Initial delay (mins)(Id): 14
End of Run (mins)(ER): 95
Baseline Times(mins)(Bb,Eb): 15.38
Data Proc Times(Bp,Ep): 15.5,37
FILE NAME? SEC BITUMEN
TIME FUNCTIONS...
RUN TIME:TT?
Universal Calibration (Y/N)(UC): N
Standards Table...
Elution Time(RT): 19.68
Mol.Wt.(MW): 30100
Elution Time(RT): 21.12
Mol.Wt.(MW): 9880
Elution Time(RT): 24.99
Mol.Wt.(MW): 4000
Elution Time(RT): 25.82
Mol.Wt.(MW): 2800
Elution Time(RT): 27.83
Mol.Wt.(MW): 955
Elution Time(RT): 29.54
Mol.Wt.(MW): 578
Elution Time(RT): 28.77
Mol.Wt.(MW): 395
Elution Time(RT): 30.83
Mol.Wt.(MW): 308
Elution Time(RT): 29.68
Mol.Wt.(MW): 283
Elution Time(RT): 31.98
Mol.Wt.(MW): 278
Elution Time(RT): 30.74
Mol.Wt.(MW): 276
Elution Time(RT): 30.84
Mol.Wt.(MW): 254
Elution Time(RT): 30.59
Mol.Wt.(MW): 252
Elution Time(RT): 30.51
Mol.Wt.(MW): 228
Elution Time(RT): 30.34
Mol.Wt.(MW): 226
Elution Time(RT): 31.14
Mol.Wt.(MW): 202
Elution Time(RT): 31.46
Mol.Wt.(MW): 192
Elution Time(RT): 31.35
Mol.Wt.(MW): 178
Elution Time(RT): 32.09
Mol.Wt.(MW): 170
Elution Time(RT): 32.62
Mol.Wt.(MW): 167
Elution Time(RT): 31.66
Mol.Wt.(MW): 166
Elution Time(RT): 32.24
Mol.Wt.(MW): 156
FIT Type(0=PL to PL,1=linear,2=quad,3=cubic)(FL):
Cal Plot(Y/N): Y
END OF DIALOG
RUN
```

Sum Errors Sqrd= 0.2249259 Coeff of Determ= 0.97225
Fit:Y=A+B*X+C*X^2+D*X^3 A= 7.864983&8= -.1775874C= 0. D= 0.
GPC Cal Rel Time vs. log MW

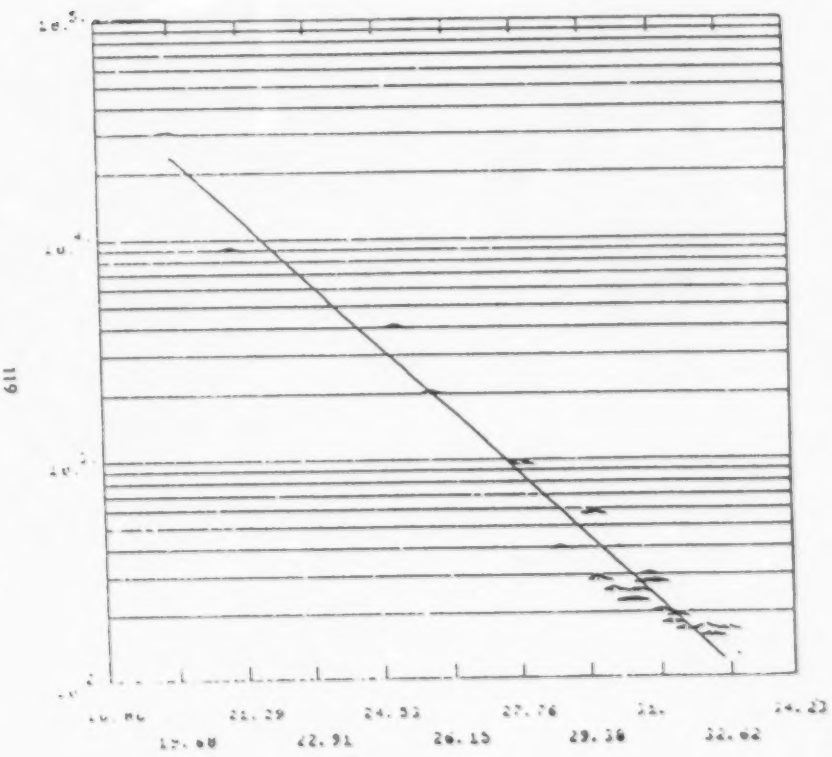
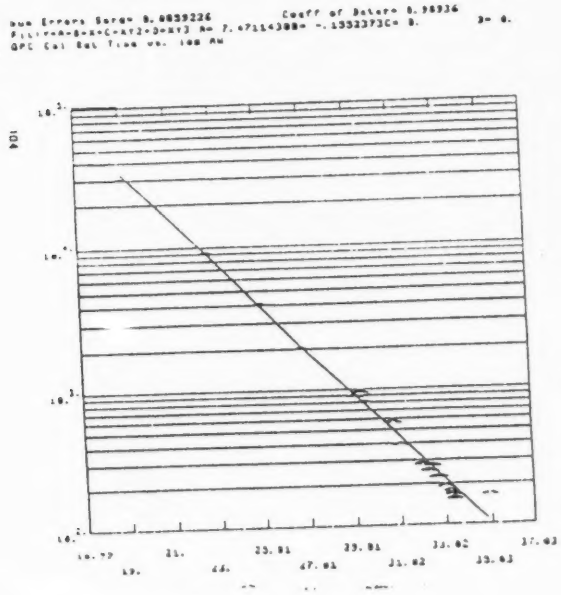
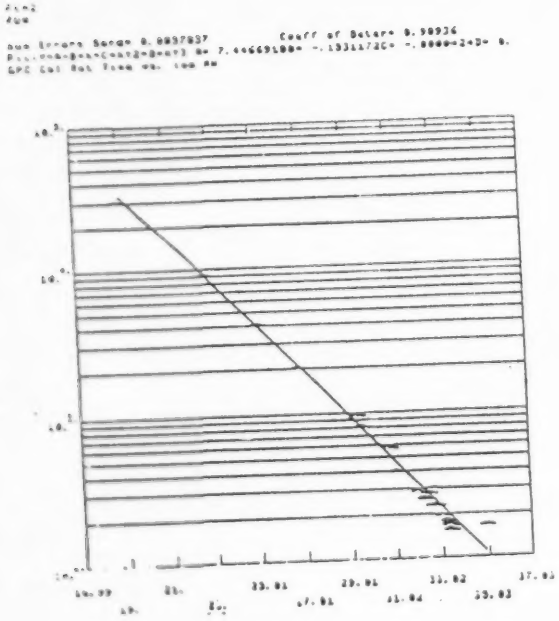


FIGURE 18

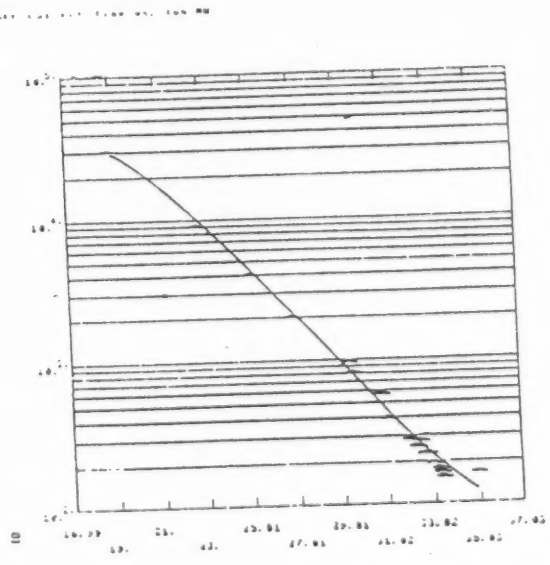
Linear Calibration (log MW/Retention Time)
of 22 Model Compounds in 2 x PSM 60-S/o-Xylene/
35°C/0.3 mL/min for Analysis of Heavy Crude Samples
(Data in Table 12)



Linear



Cubic



Quadratic

FIGURE 19

Linear, Cubic and Quadratic Calibration
(log MW/Retention Time) of 25 Model Compounds
in 2 x PSM 60-S/o-Xylene/35°C/0.3 mL/min
for Analysis of Heavy Crude Samples
(Data in Table 13)

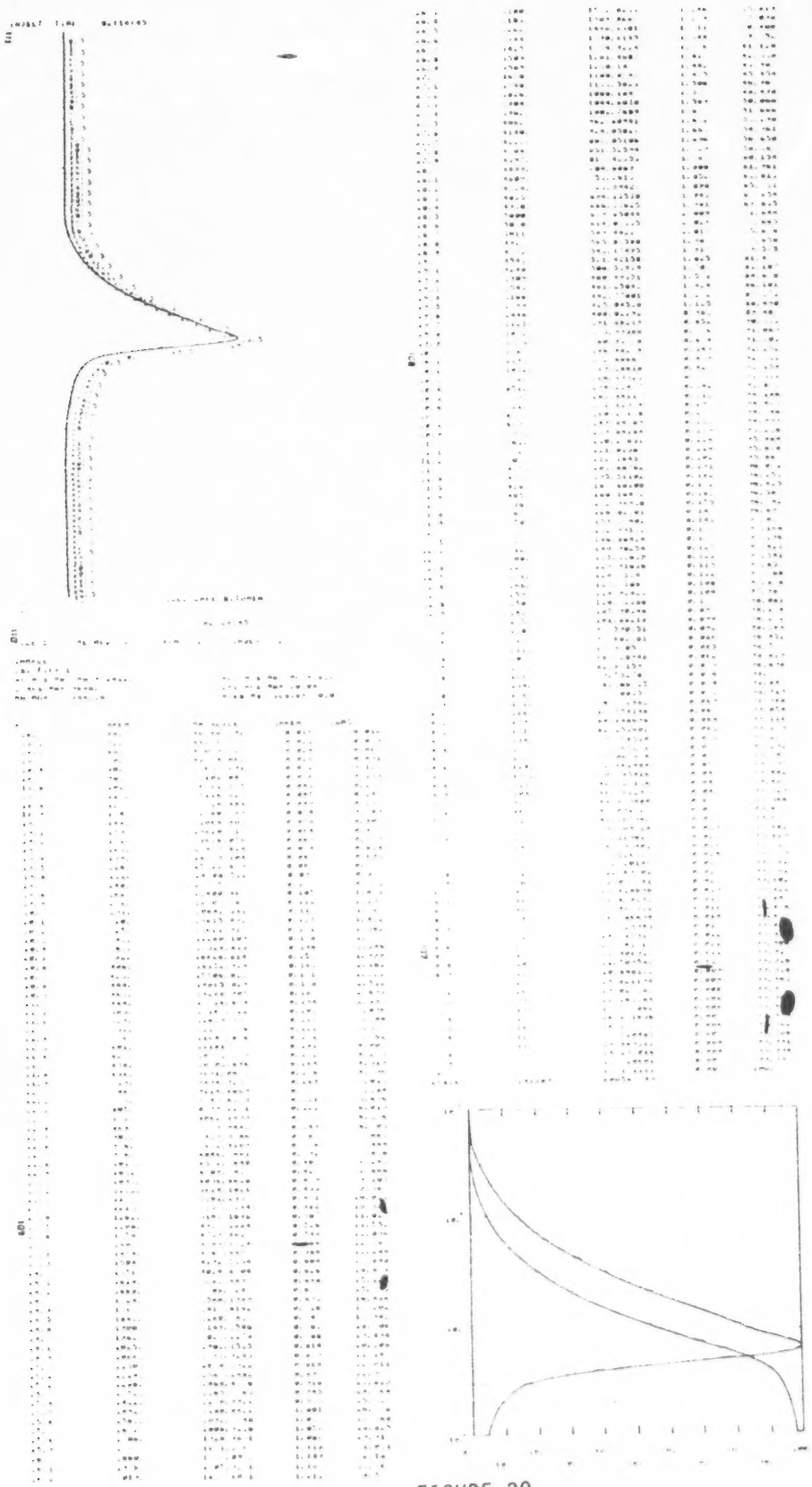
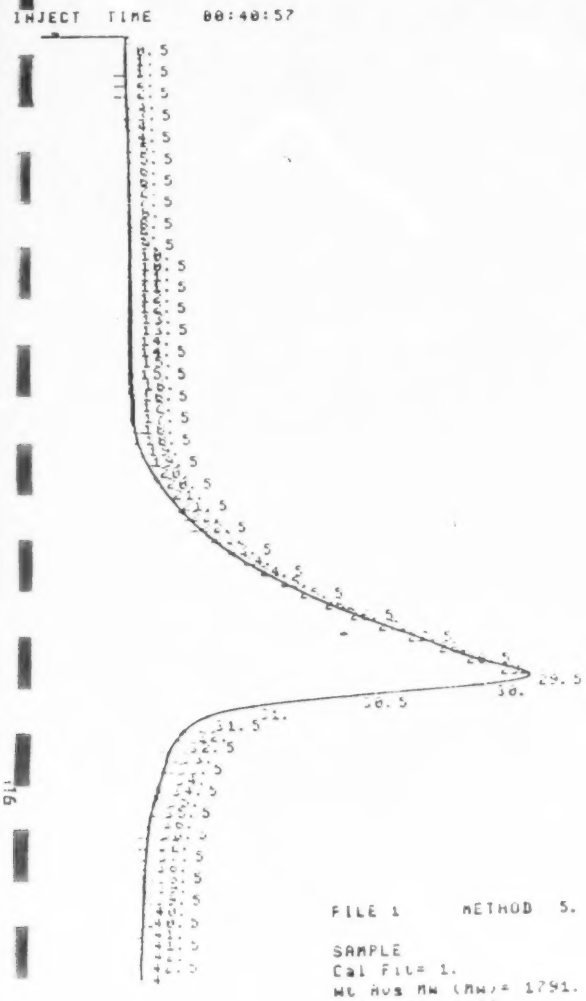
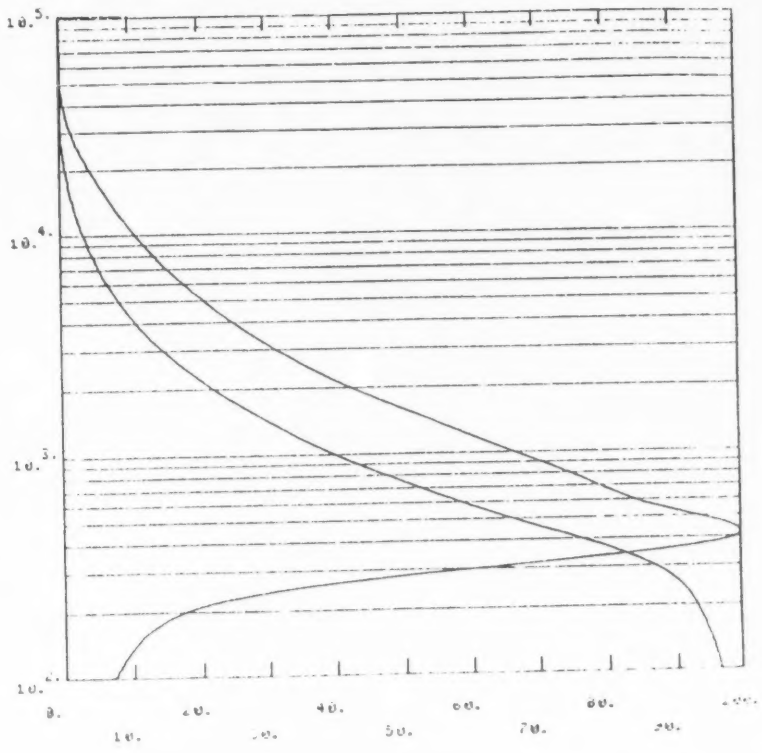


FIGURE 20

SEC Profile and MWD Normalized
and Cumulative Curves of Cold Lake Heavy Oil
2 x PSM 60-S/o-Xylene/0.3 mL/min/35°C





FILE 1 METHOD 5. RUN 1 INDEX 1

SAMPLE
Cal File= 1.
Wt Avg MW (MW)= 1791.
Z Avg MW= 7833.
MW/Mn= 4.2093311

No. Avg MW (Mn)= 425.
Z+1 Avg MW= 17514.
Area Max Scale= 5502.

RT	AREA	MW/SLICE	SAREA	CUM.
16.	14.	46748.792	0.003	0.003
16.1	16.	44870.547	0.006	0.011
16.2	23.	43079.367	0.008	0.019
16.3	28.	41354.062	0.01	0.029
16.4	27.	39697.891	0.01	0.039
16.5	35.	38106.047	0.012	0.051
16.6	42.	36581.875	0.015	0.066
16.7	49.	35116.823	0.017	0.083
16.8	57.	33710.444	0.02	0.103
16.9	67.	32360.389	0.024	0.127
19.	74.	31064.402	0.026	0.153
19.1	85.	29820.317	0.03	0.183
19.2	99.	28626.056	0.035	0.218
19.3	110.	27479.624	0.039	0.257

37.3	51.	16.[illegible]	0.018	99.905
37.4	48.	16.021656	0.017	99.941
37.5	44.	16.157572	0.016	99.957
37.6	42.	15.510485	0.015	99.952
37.7	39.	14.882344	0.014	99.966
37.8	34.	14.293016	0.012	99.977
37.9	35.	13.720681	0.012	99.99
38.	29.	13.171111	0.01	100.
Totals	283779.	508402700		

FIGURE 21

SEC Profile and MWD Normalized
and Cumulative Curves of Lloydminster Heavy Oil
2 x PSM 60-S/o-Xylene/0.3 mL/min/35°C

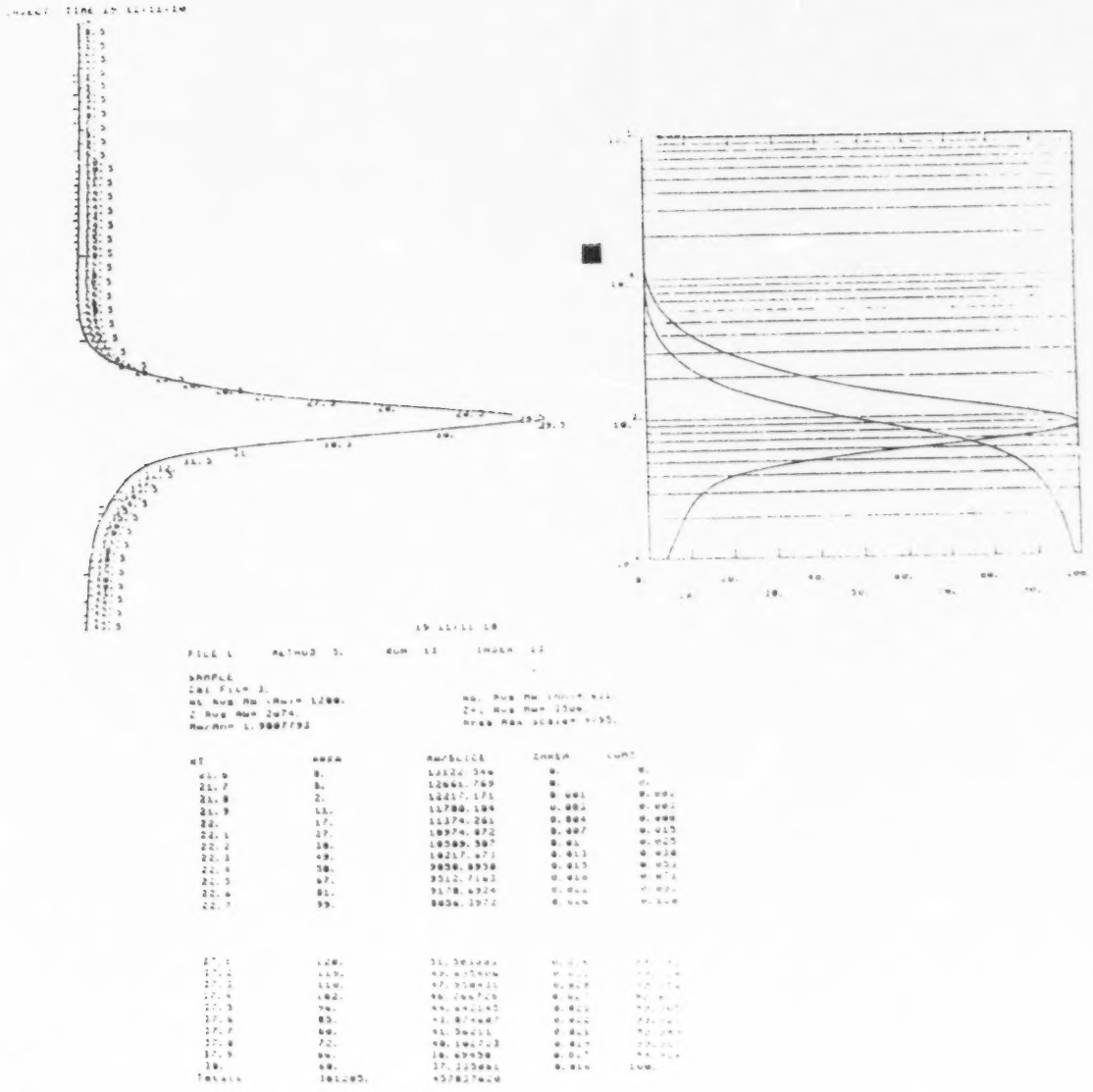
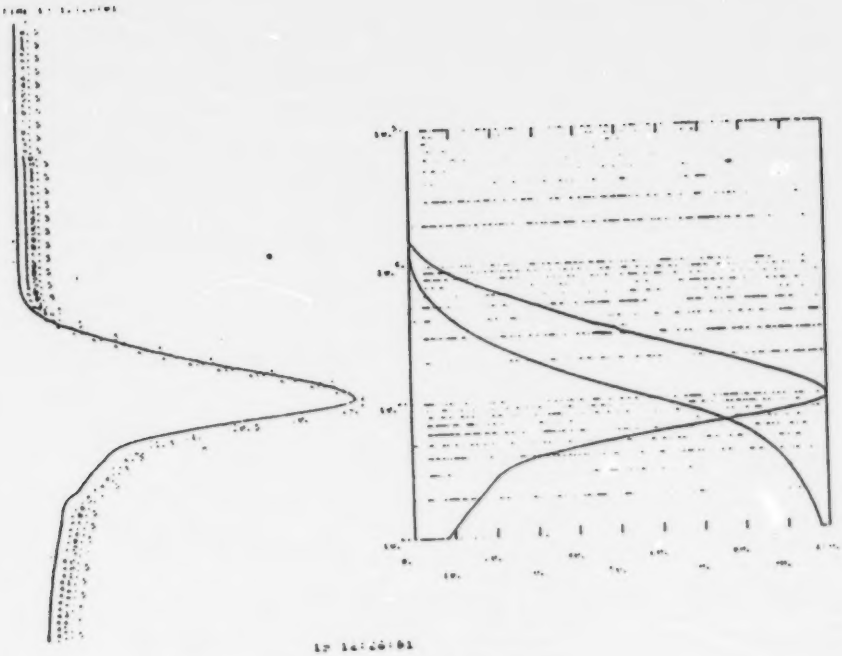


FIGURE 22

SEC Profile and MWD Normalized
and Cumulative Curves of Visbreaking Residue
2 x PSM 60-S/o-Xylene/0.3 mL/min/35°C



FILE 1 METHOD 5. RUN 14 INDEX 14

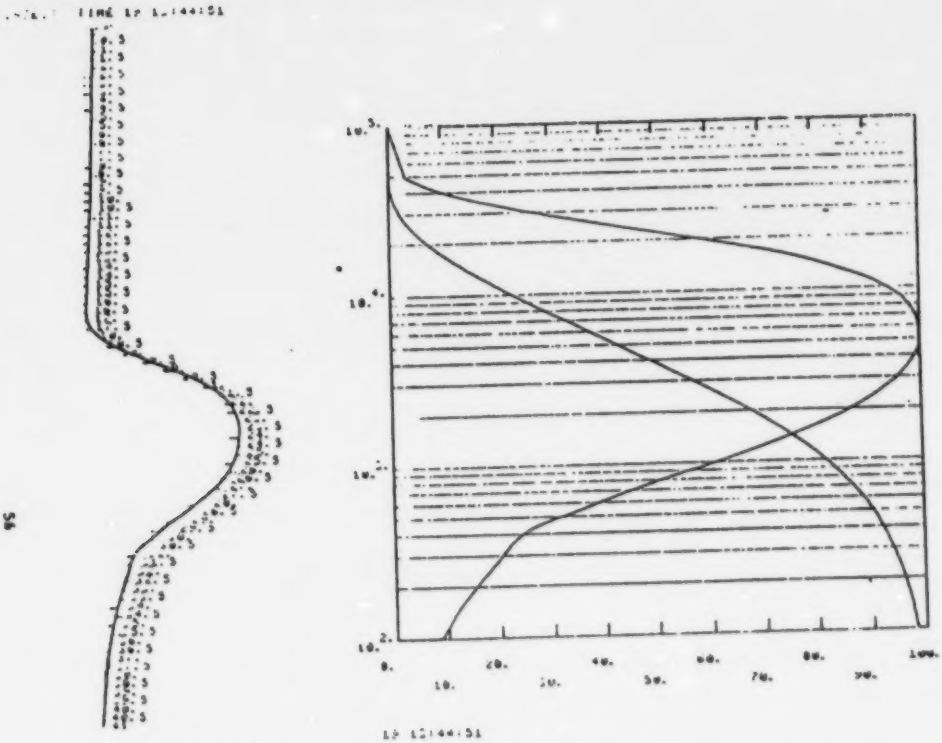
SAMPLE
Cal File 1:
WL Avg Mw (Mw/n 1726.
Z Avg Mw 1498.
Mw/Mn =.850,951

No. Avg Mw (Mn/n 651.
Z=1 Avg Mw 5622.
Area Mws Scale= 7240.

RT	AREA	MW/SLICE	%AREA	%CUM
20.9	0.	16853.474	0.	0.
21.	0.	16283.496	0.	0.
21.1	9.	15678.497	0.006	0.006
21.2	25.	15139.551	0.009	0.015
21.3	43.	14607.951	0.01	0.025
21.4	66.	14095.816	0.015	0.039
21.5	92.	13600.692	0.021	0.059
21.6	117.	13122.546	0.017	0.076
21.7	147.	12661.769	0.074	0.149
21.8	188.	12217.171	0.041	0.190
21.9	216.	11788.184	0.05	0.240
22.	297.	11374.261	0.059	0.299
22.1	194.	51.581065	0.042	99.744
22.2	178.	49.695486	0.041	99.752
22.3	168.	47.950431	0.039	99.79
22.4	157.	46.296748	0.037	99.867
22.5	151.	44.644145	0.035	99.894
22.6	140.	43.074007	0.032	99.924
22.7	120.	41.56611	0.02	99.944
22.8	112.	40.102761	0.027	99.971
22.9	110.	38.69438	0.025	99.997
23.	101.	37.335081	0.023	100.
Totals	4241461.	7e+982192		

FIGURE 23

SEC Profile and MWD Normalized and Cumulative Curves of Visbreaking C_7 Asphaltene 2 x PSM 60-S/o-Xylene/0.3 mL/min/35°C



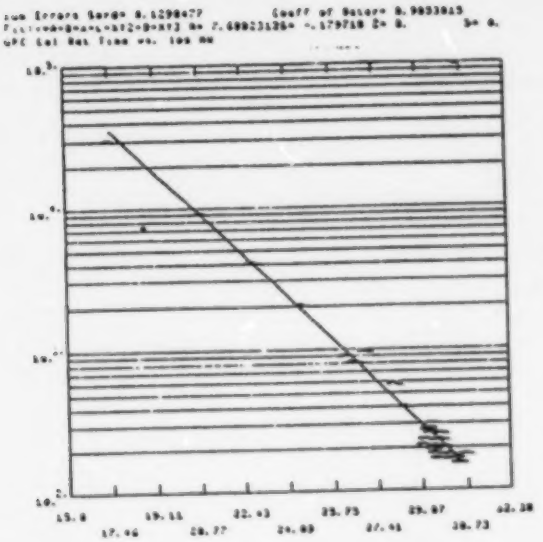
FILE 1 METHOD 3. RUN 15 INDEX 15

SAMPLE

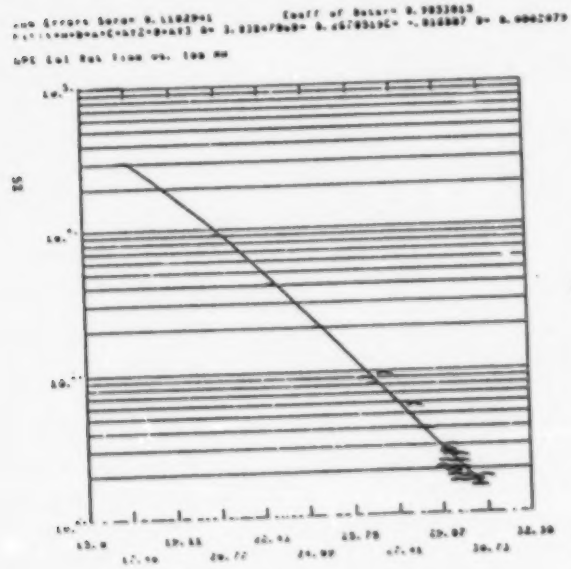
VT	WDEN	RW/SLICE	CWDEN	CUMU
18.	85.	47519.556	0.022	0.022
18.1	110.	45850.344	0.044	0.014
18.2	138.	44241.	0.052	0.107
18.3	169.	42667.547	0.065	0.172
18.4	202.	41160.641	0.078	0.250
18.5	240.	39744.000	0.092	0.342
19.	79.	38.378176	0.040	99.740
19.1	76.	51.302002	0.035	99.782
19.2	85.	49.925400	0.040	99.815
19.3	81.	47.750421	0.021	99.840
19.4	74.	46.266720	0.020	99.874
19.5	69.	44.642145	0.026	99.901
19.6	65.	43.074007	0.023	99.940
19.7	59.	41.56211	0.023	99.940
19.8	52.	40.102721	0.02	99.980
19.9	44.	38.69438	0.017	99.995
20.	40.	37.335001	0.015	100.
Totals	2613210.	9.1003T+10		

FIGURE 24

SEC Profile and MWD Normalized and
Cumulative Curves of Lloydminster C_7 Asphaltene
2 x PSM 60-S/o-Xylene/0.3 mL/min/35°C



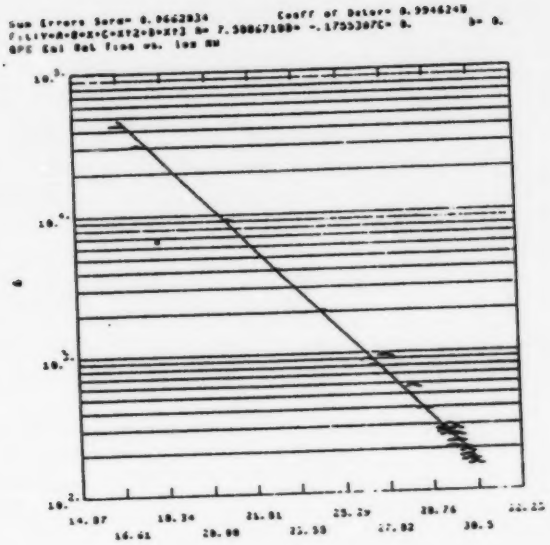
Linear



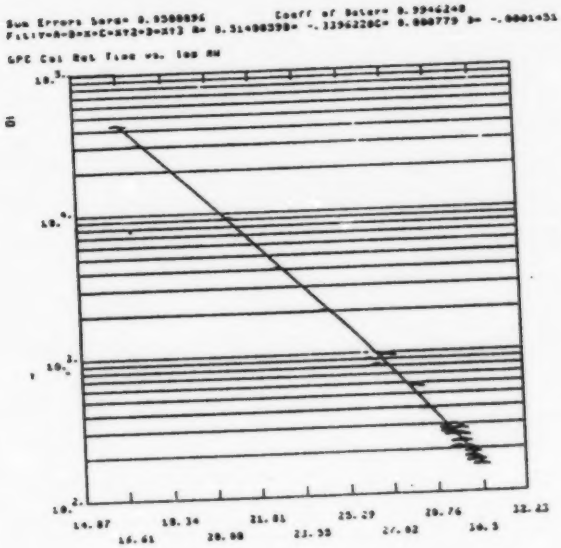
Cubic

FIGURE 25

Linear and Cubic Calibration (log MW/Retention Time)
of 34 Model Compounds in 2 x PSM 60-S/THF/35°C/
0.3 mL/min for Analysis of Heavy Crude Samples
(Data in Table 16 excluding PS 42,800)



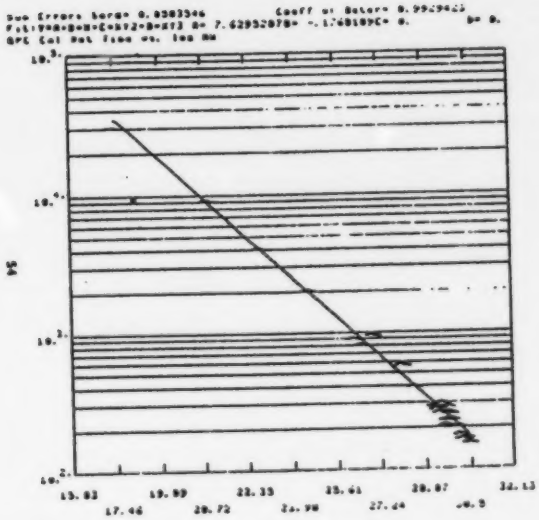
Linear



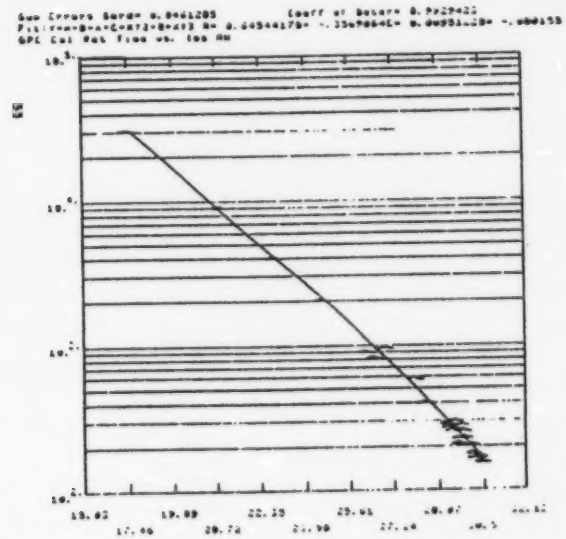
Cubic

FIGURE 26

Linear and Cubic Calibration (log MW/Retention Time)
of 29 Model Compounds in 2 x PSM 60-S/THF/35°C/
0.3 mL/min
(Data in Table 16 excluding Pyrene Carboxaldehyde,
Phen. Quinone, Phenanthrol, Hydroxy Fluorene,
Acridine and Carbazole)



Linear



Cubic

FIGURE 27

Linear and Cubic Calibration (log MW/Retention Time) of 28 Model Compounds in 2 x PSM 60-S/THF/35°C/ 0.3 mL/min for Analysis of Heavy Crude Samples (Data in Table 16 excluding PS 42,800, Pyrene Carboxaldehyde, Phen. Quinone, Phenanthrol, Hydroxy Fluorene, Acridine and Carbazole)

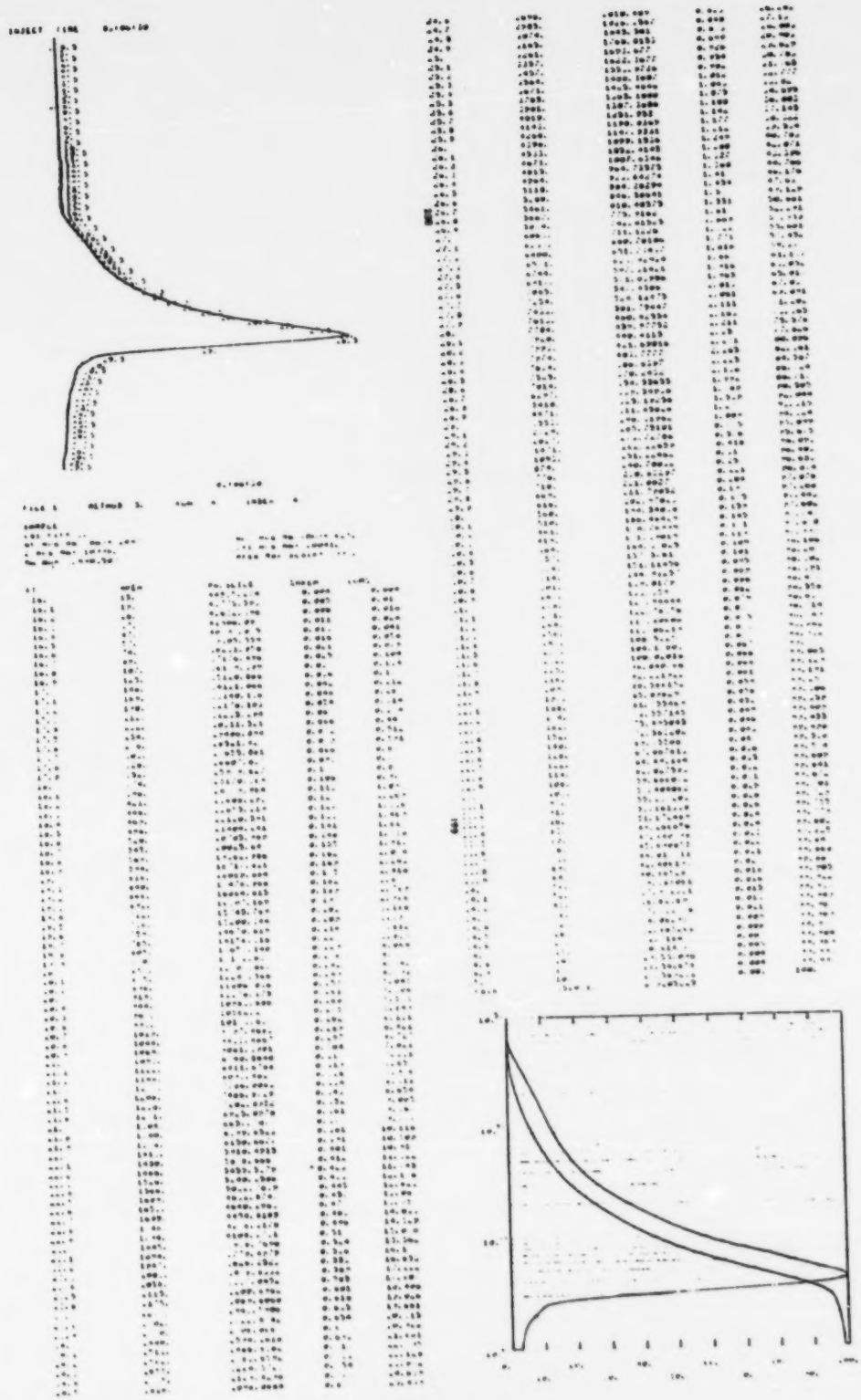
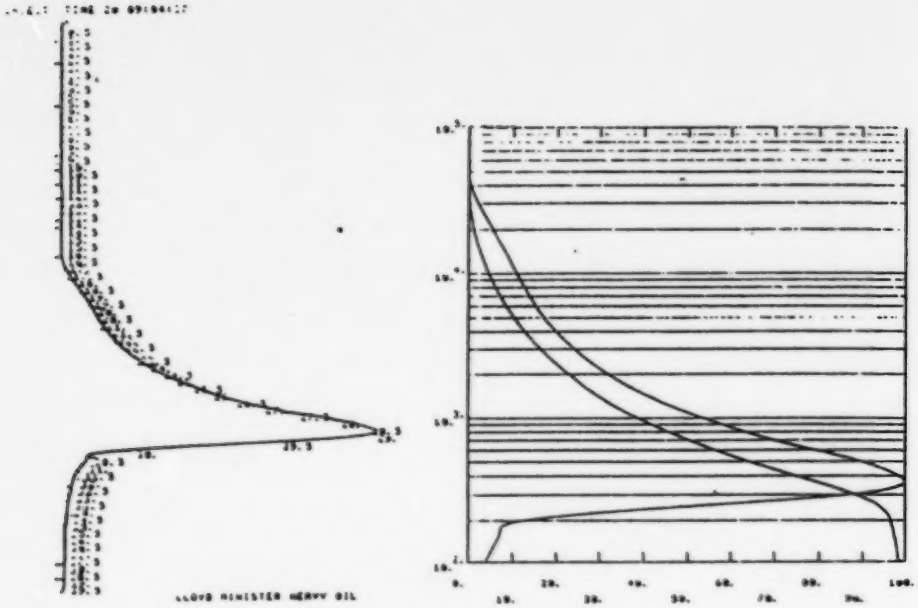


FIGURE 28

SEC Profile and MWD Normalized
and Cumulative Curves of Cold Lake Heavy Oil
2 x PSM 60-S/THF/0.3 mL/min/35°C



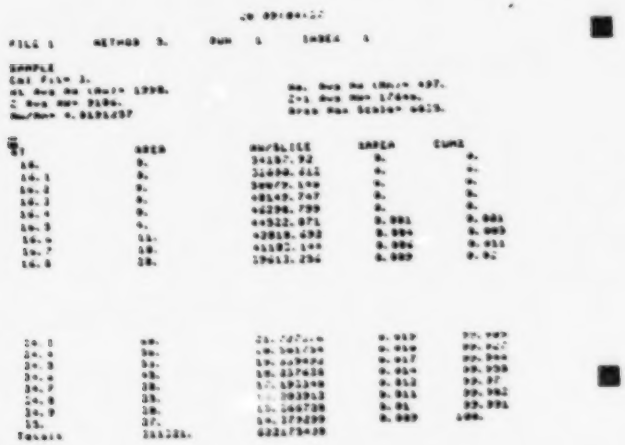


FIGURE 29

SEC Profile and MWD Normalized and Cumulative Curves of Lloydminster Heavy Oil 2 x PSM 60-S/THF/0.3 mL/min/35°C

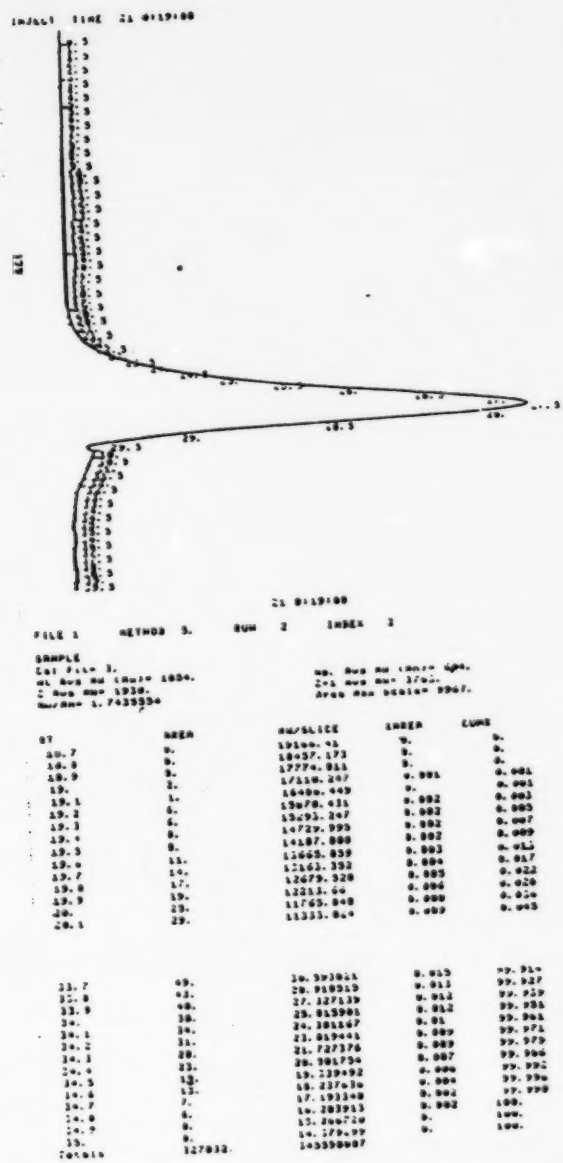
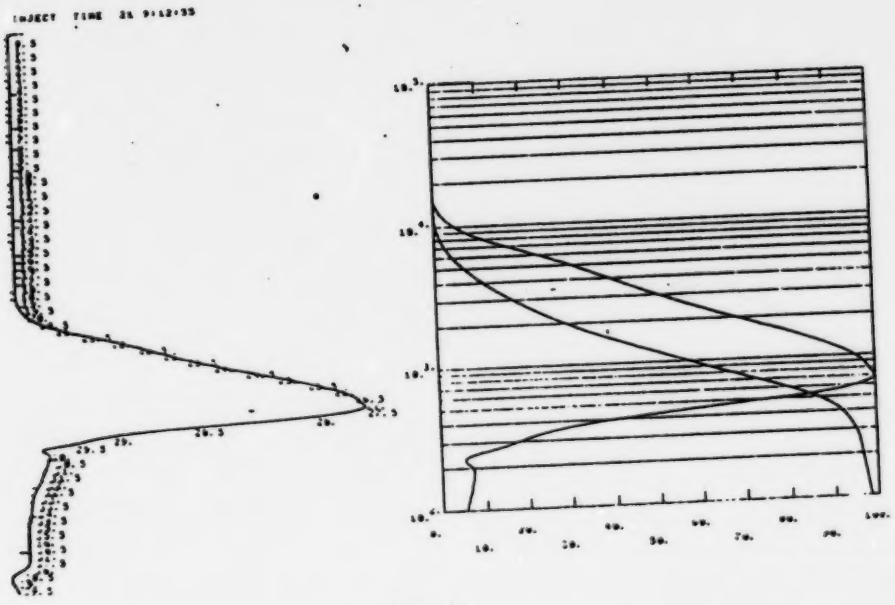


FIGURE 30

SEC Profile of Visbreaking Residue 2 x PSM 60-S/THF/0.3 mL/min/35°C



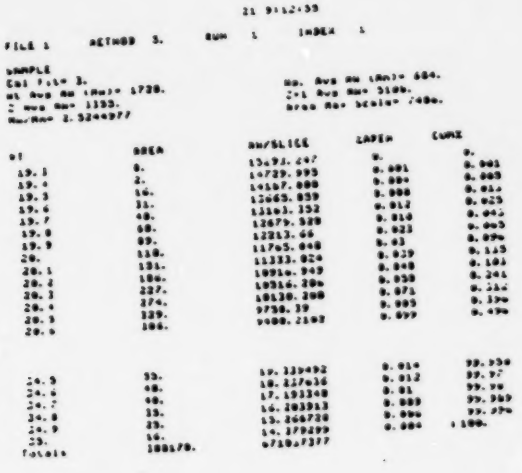


FIGURE 31

SEC Profile and MWD Normalized
and Cumulative Curves of Visbreaking C_7 Asphaltene
2 x PSM 60-S/THF/0.3 mL/min/35°C

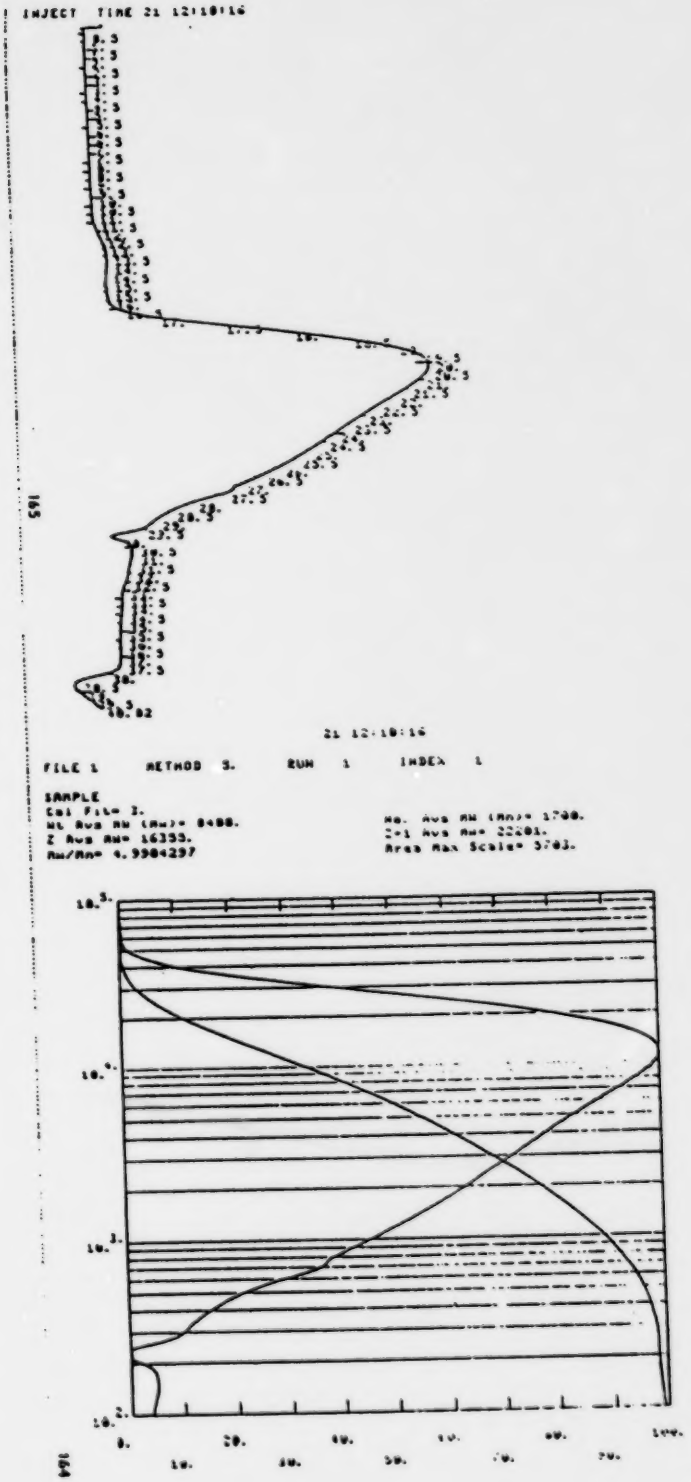
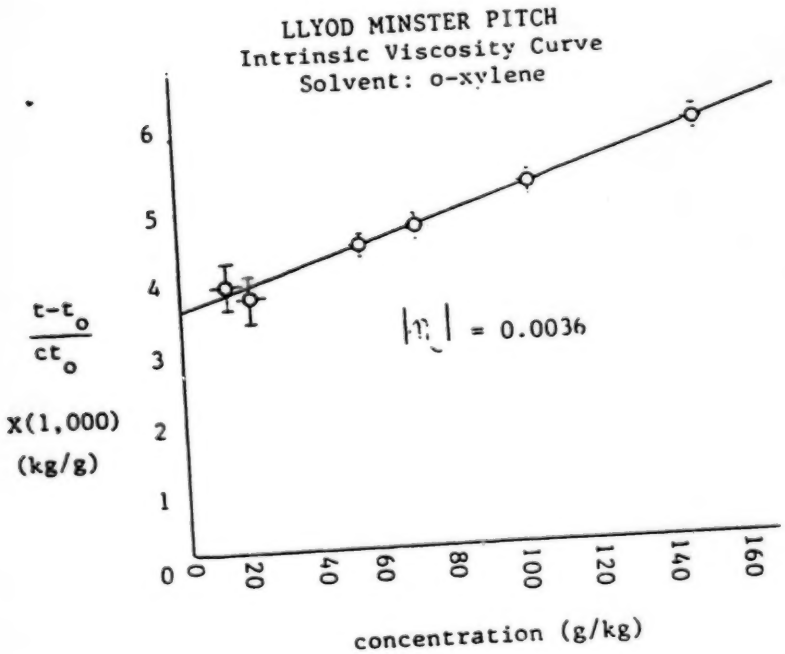


FIGURE 32

SEC Profile and MWD Normalized and Cumulative Curves of Lloydminster C_7 Asphaltene 2 x PSM 60-S/THF/0.3 mL/min/35°C

FIGURE 33

Intrinsic Viscosity Curve
Lloydminster Heavy Oil in o-Xylene

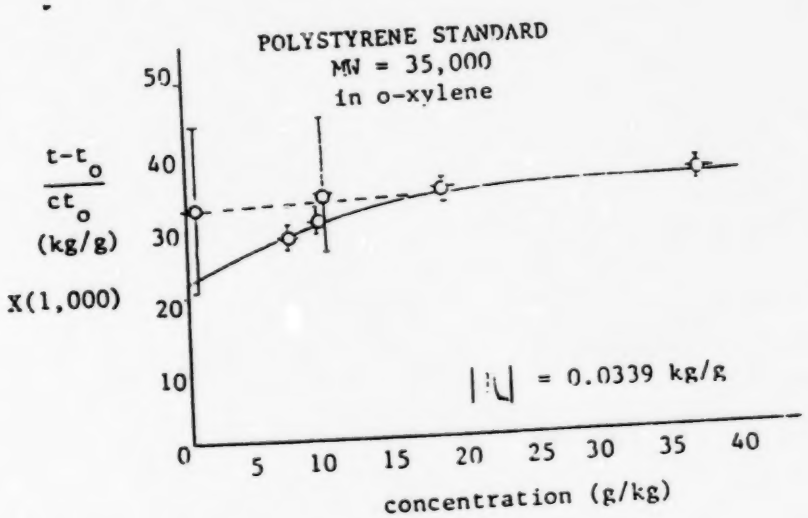


conc'n (g/kg)	t (sec)	$\frac{t-t_o}{ct_o}$ (kg/g)
12.6	478.6	0.0039
20.3	490.1	0.0037
52.2	561.4	0.0044
69.1	601.6	0.0046
101.7	697.3	0.0052
150.9	865.0	0.0059

t_o = 456.2 sec

FIGURE 34

Intrinsic Viscosity Curve
Polystyrene Standard (MW 35,000) in o-Xylene

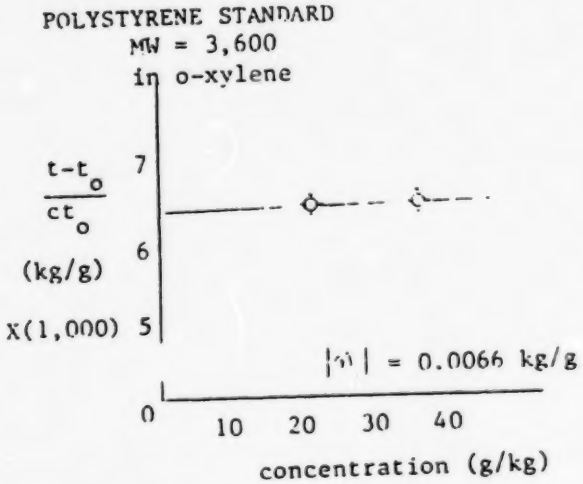


conc'n (g/kg)	t (sec)	$\frac{t-t_o}{ct_o}$ (kg/g)
37.5	1,057.7	0.0359
18.8	746.6	0.0349
10.1	155.1	0.0340
9.8	135.6	0.0307
0.8	11.7	0.0324

t_o = 451 sec

FIGURE 35

Intrinsic Viscosity Curve
Polystyrene Standard (MW 3600) in o-Xylene



NOTE: 1. Not enough sample for more concentrated solutions.
2. Further dilution caused inconsistant results.

conc'n (g/kg)	t (sec)	$\frac{t-t_o}{ct_o}$ (kg/g)
37.5	5[illegible].2	0.0066
22.0	516.8	0.0066

t_o = 451 sec

Figure 36A: SEC Profiles of Model Compounds - Polystyrenes
Conditions: 10^3A^o + $500A^o$ + $500A^o$ Ultrastyragel/o-xylene/
60^oC/0.5 ml/min (Retention Time Data in Table 8)

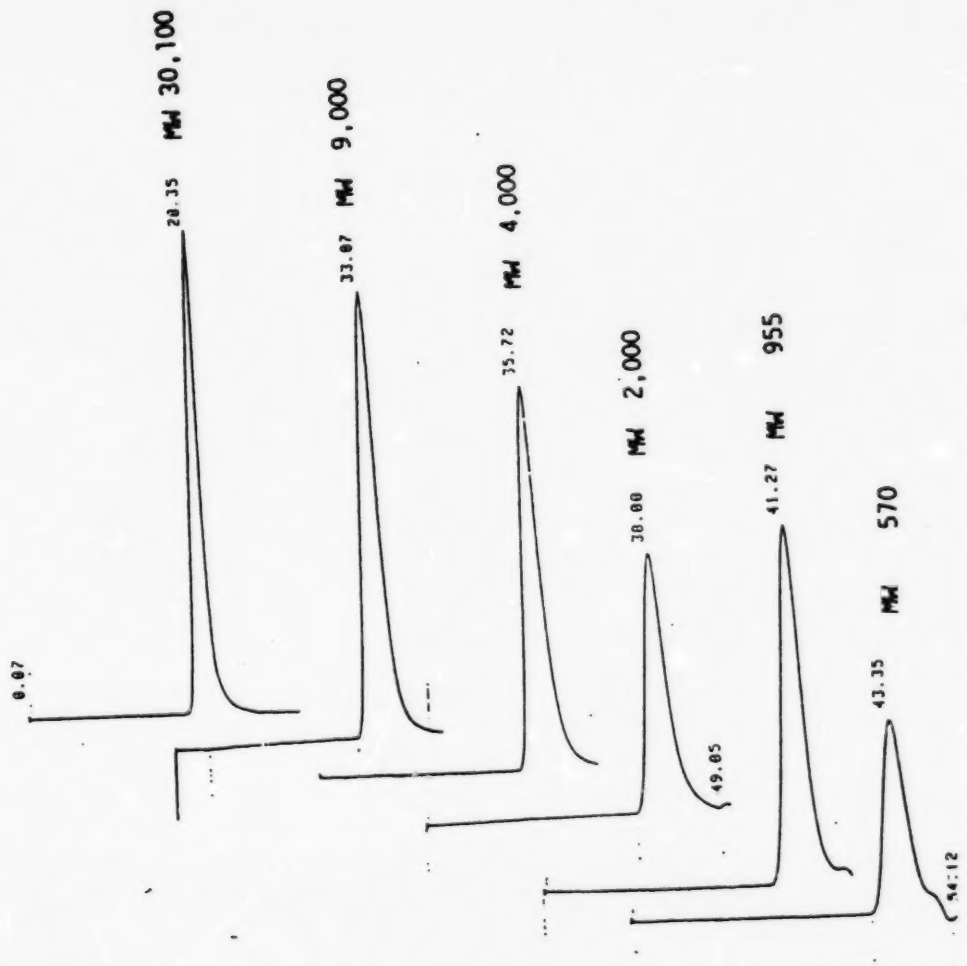


Figure 36B: SEC Profiles of Model Compounds - PNA(3 ring or less)
Conditions: 10^3A^0 + $500A^0$ Ultrastyragel/o-xylene/
60^0C/0.5 ml/min (Retention Time Data in Table 8)

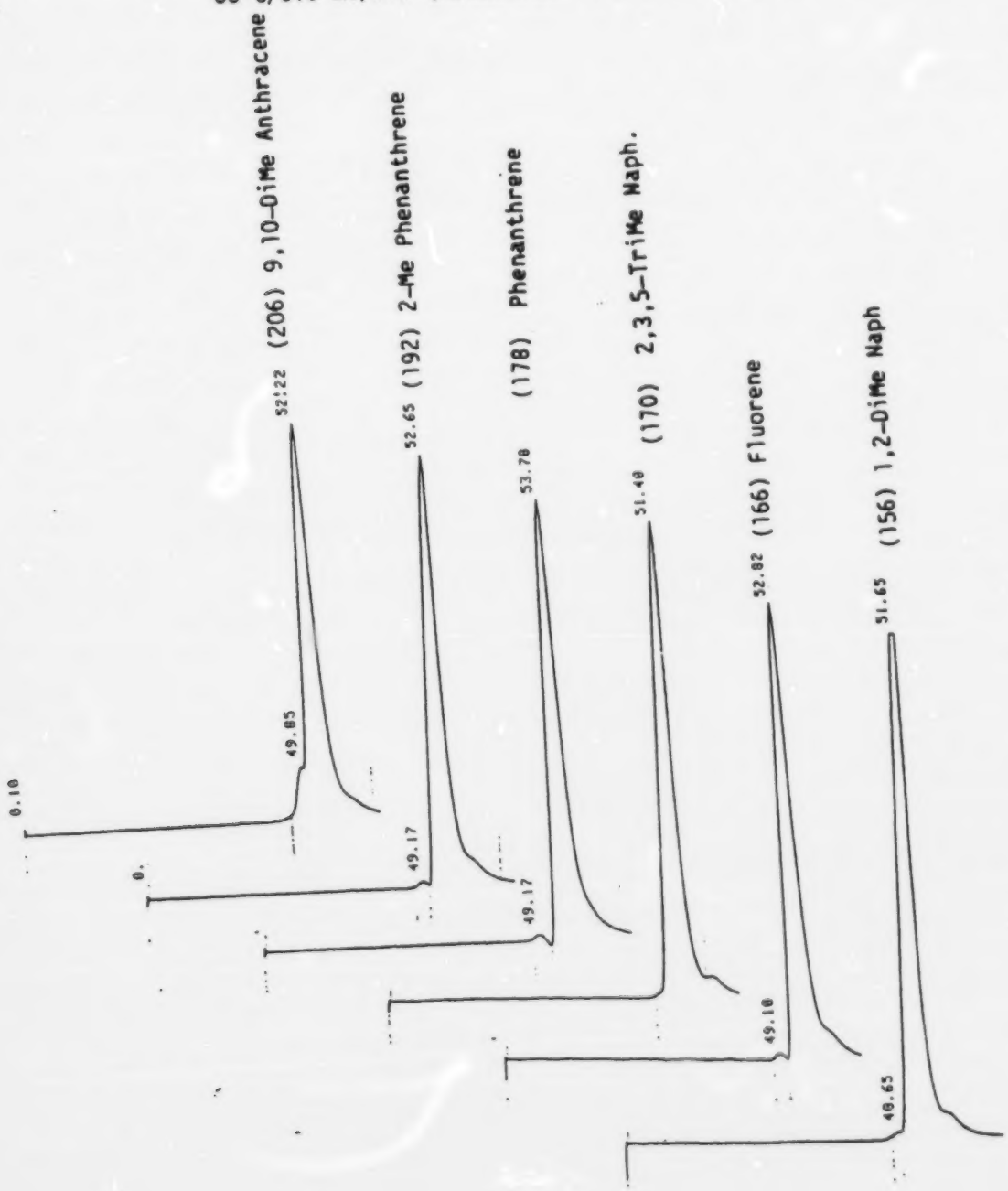


Figure 36C: SEC Profiles of Model Compounds - PNA (4 ring or more)
Conditions: 10^3A^o + $500A^o$ Ultrastyragel/o-xylene/
60^oC/o.5 ml/min (Retention Time Data in Table 8)

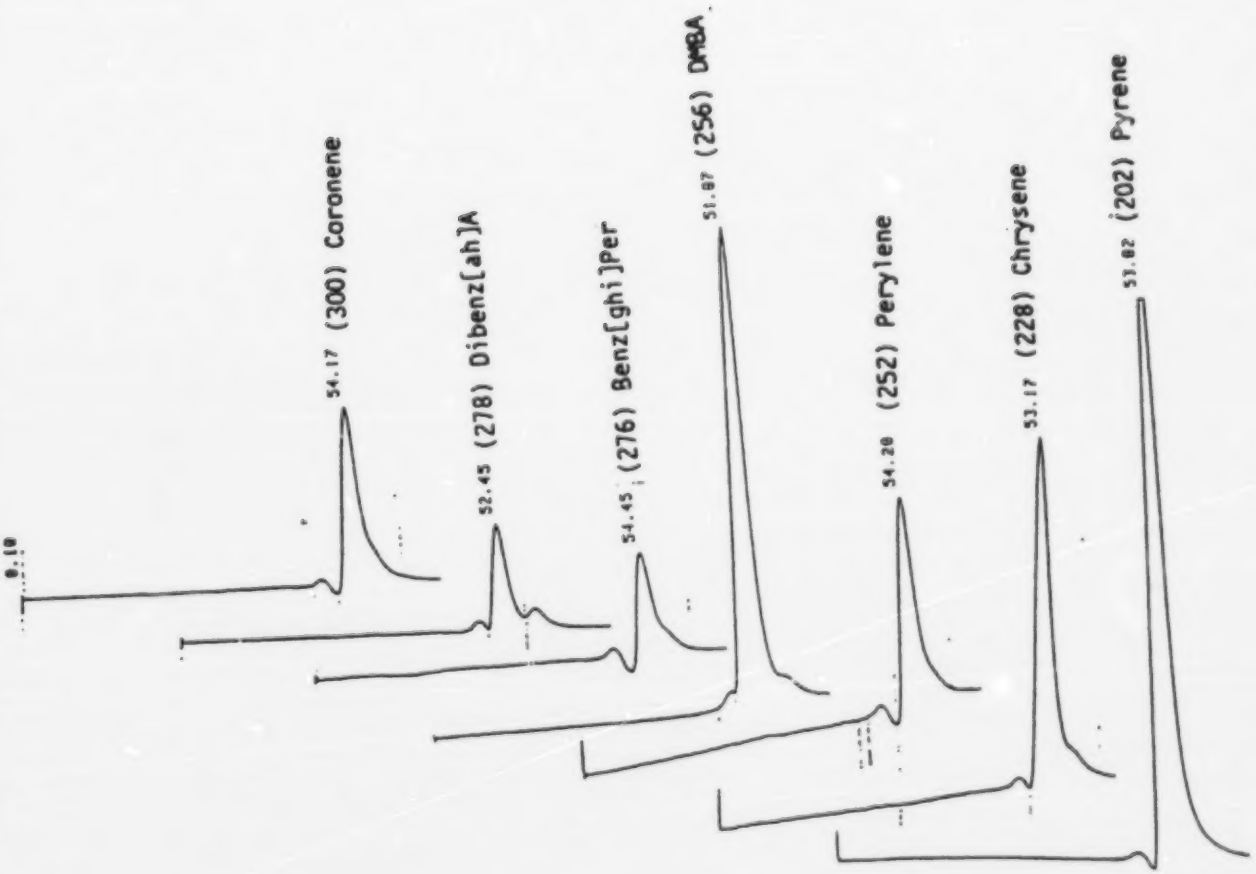


Figure 36D: SEC Profiles of Model Compounds - NPNA
Conditions: 10^3A^o + $500A^o$ + $500A^o$ Ultrastyragel/o-xylene/
60°C/0.5 ml/min (Retention Time Data in Table 8)

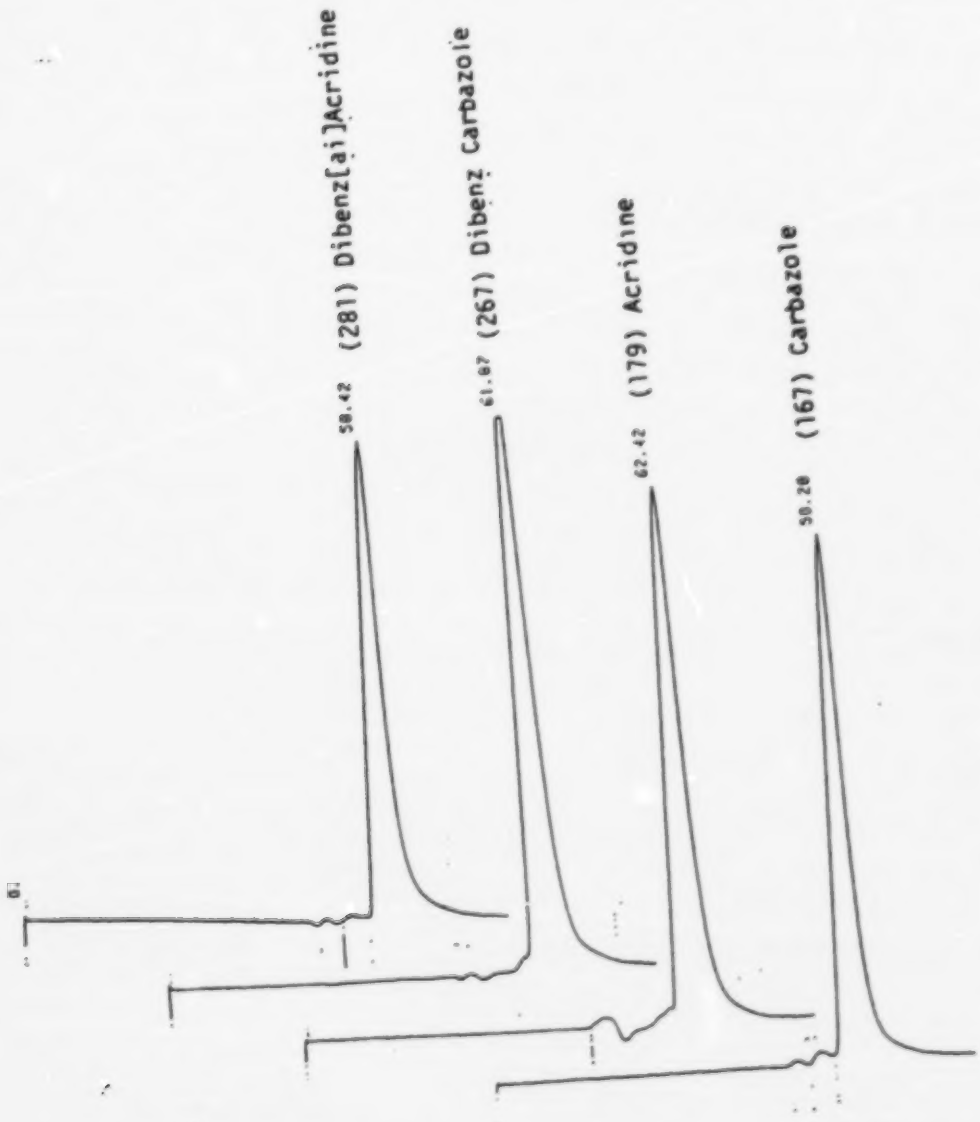


Figure 36E: SEC Profiles of Model Compounds - OPNA
Conditions: 10^3A^0 + $500A^0$ + $500A^0$ Ultrastyragel/o-xylene
60^0C/0,5 ml/min (Retention Time Data in Table 8)

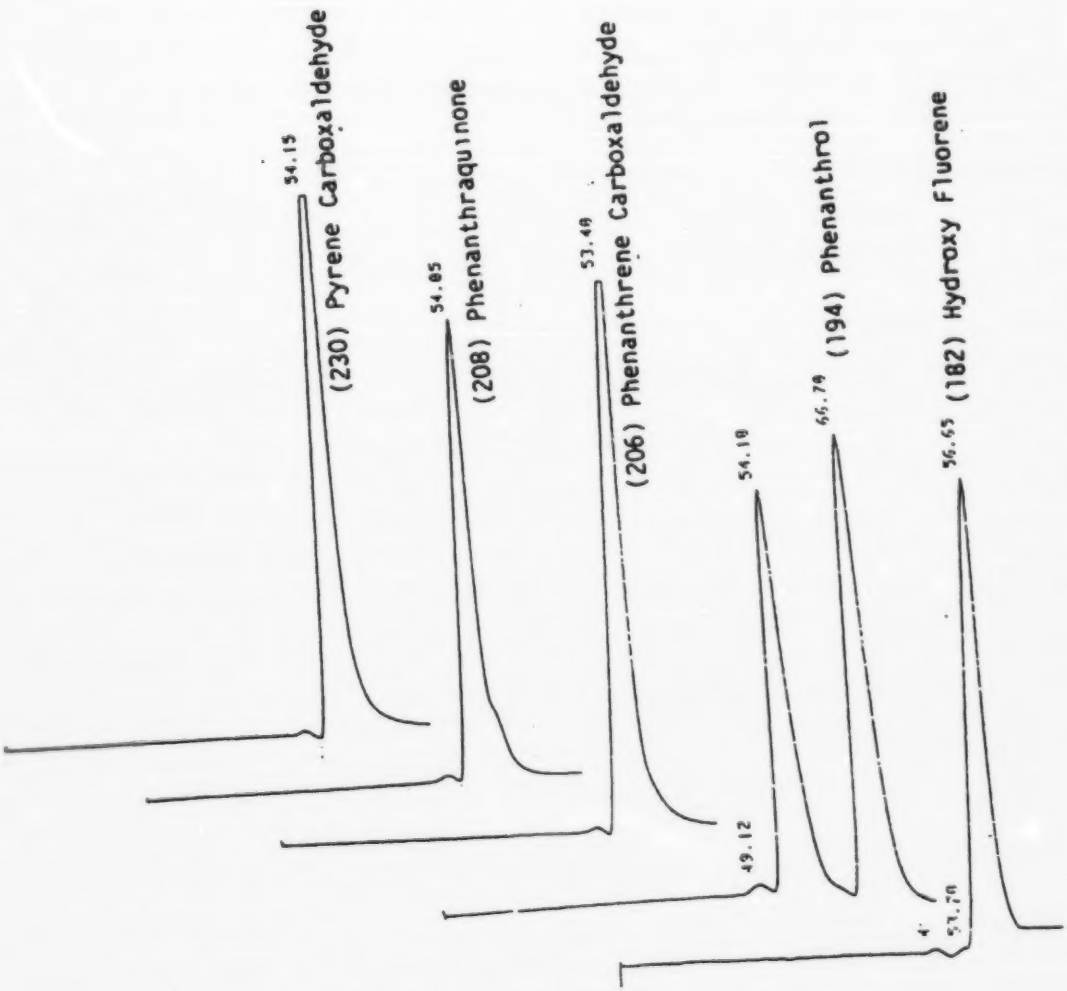


Figure 36F: SEC Profiles of Model Compounds - Saturates
Conditions: 10^3A^o + $500A^o$ + $500A^o$ Ultrastyragel/o-xylene/
60°C/0.5 ml/min (Retention Time Data in Table 8)

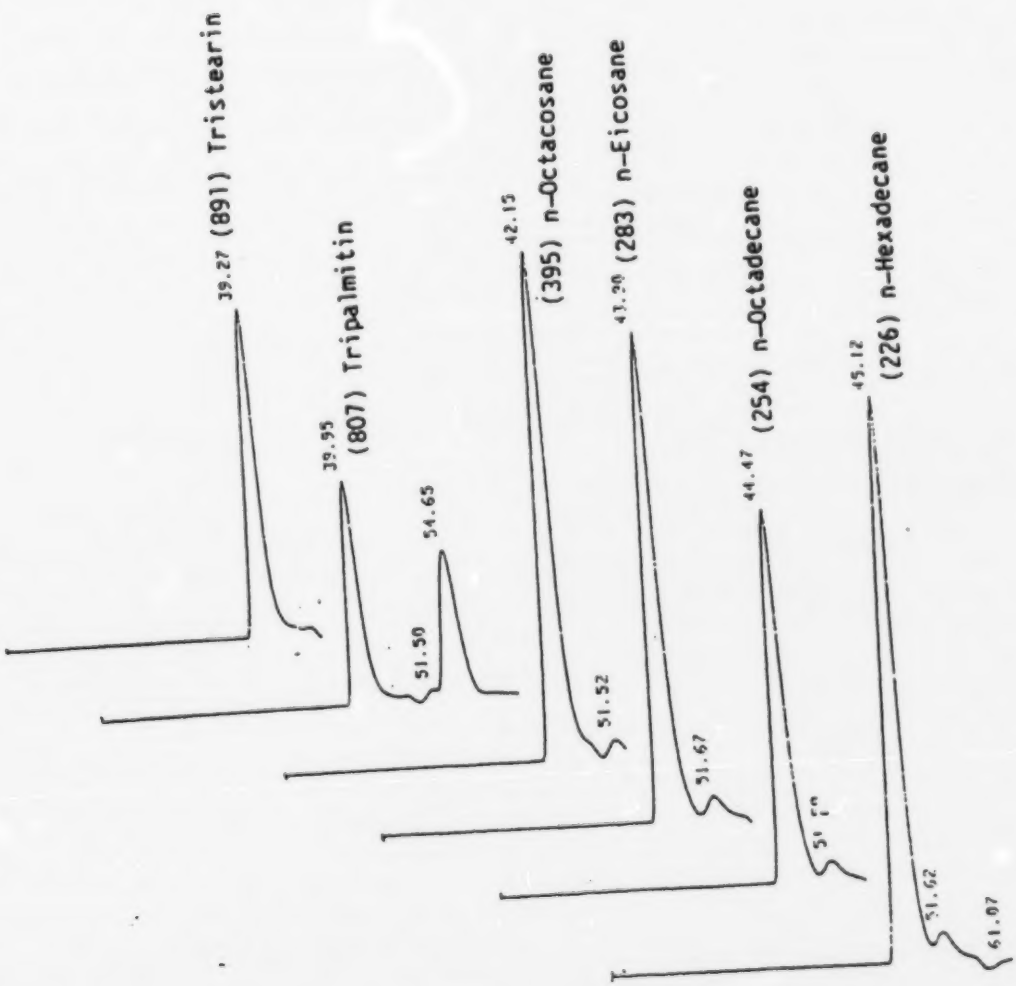


Figure 37A: SEC Profiles of Model Compounds - Polystyrenes
. Conditions: 2 x zorbax PSM 60-S/O - xylene/35°C/
0.3 ml/min (Retention Time Data in Table 13)

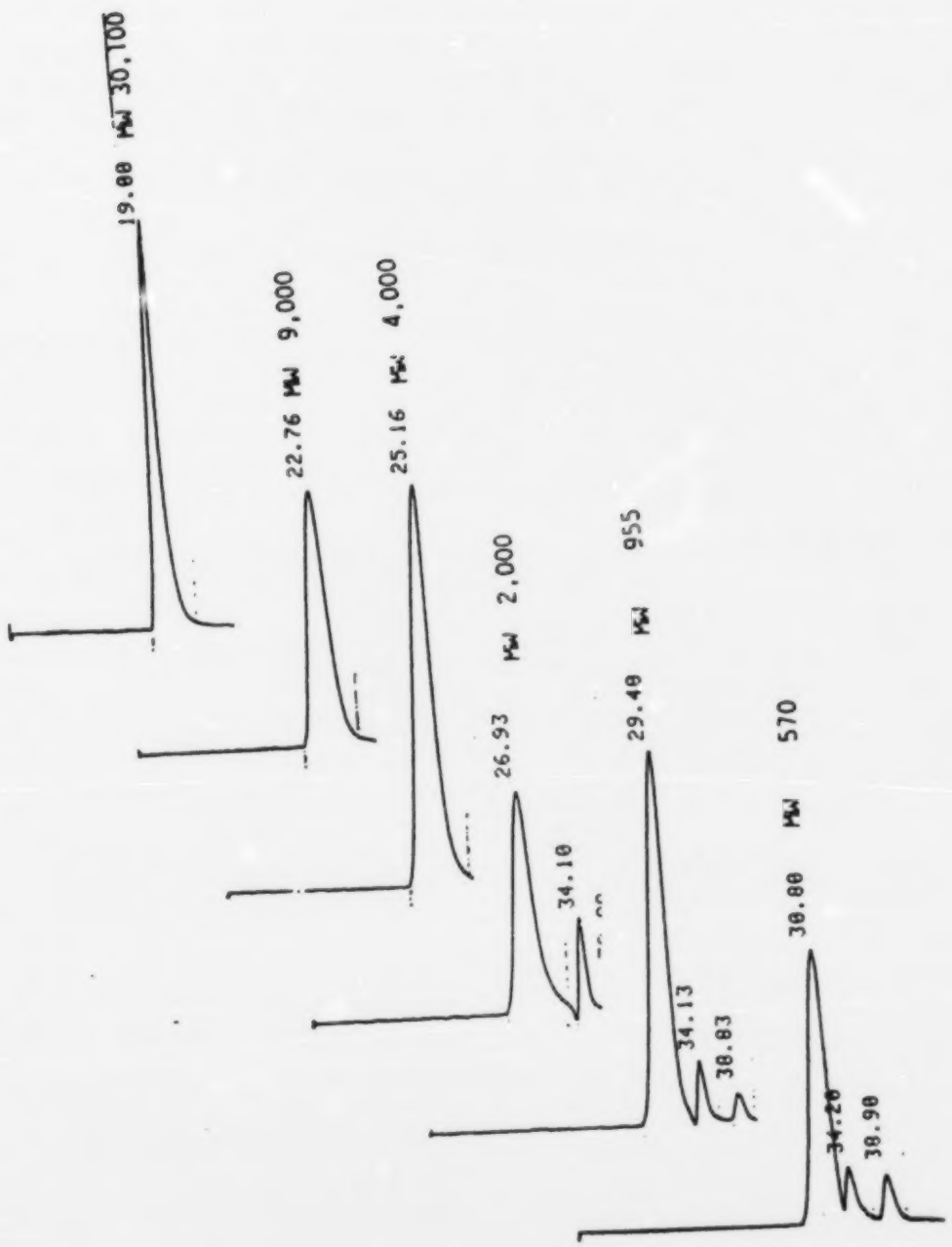


Figure 37B: SEC Profiles of Model Compounds - PNA (3 ring or less)
Conditions: 2 x zorbax PSM 60-S/O-xylene/35°C/
0.3 ml/min (Retention Time Data in Table 13)

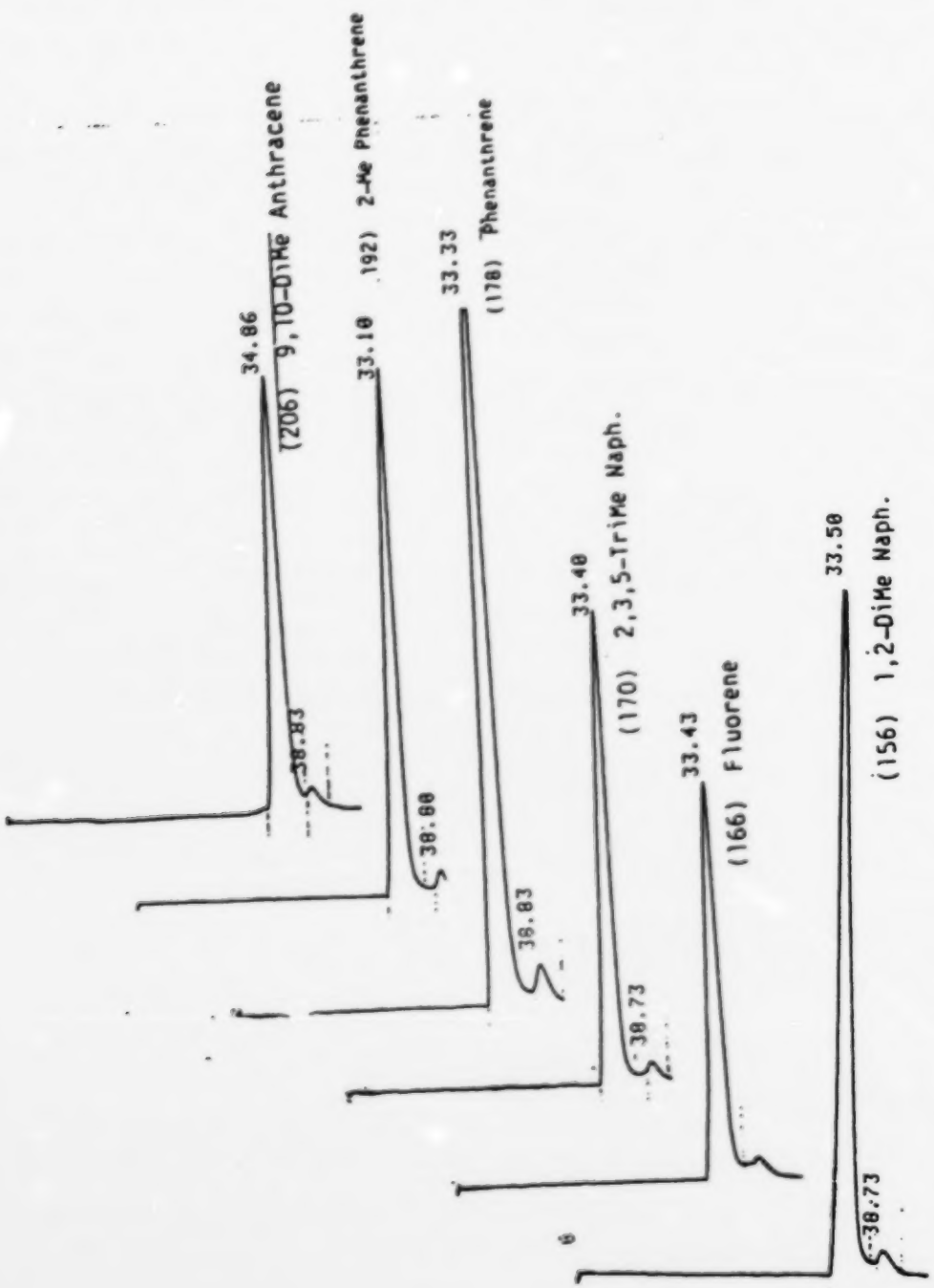


Figure 37C: SEC Profiles of Model Compounds - PNA (4 ring or more)
Conditions: 2 x zorbax PSM 60-S/O - xylene/35°C/
0.3 ml/min (Retention Time Data in Table 13)

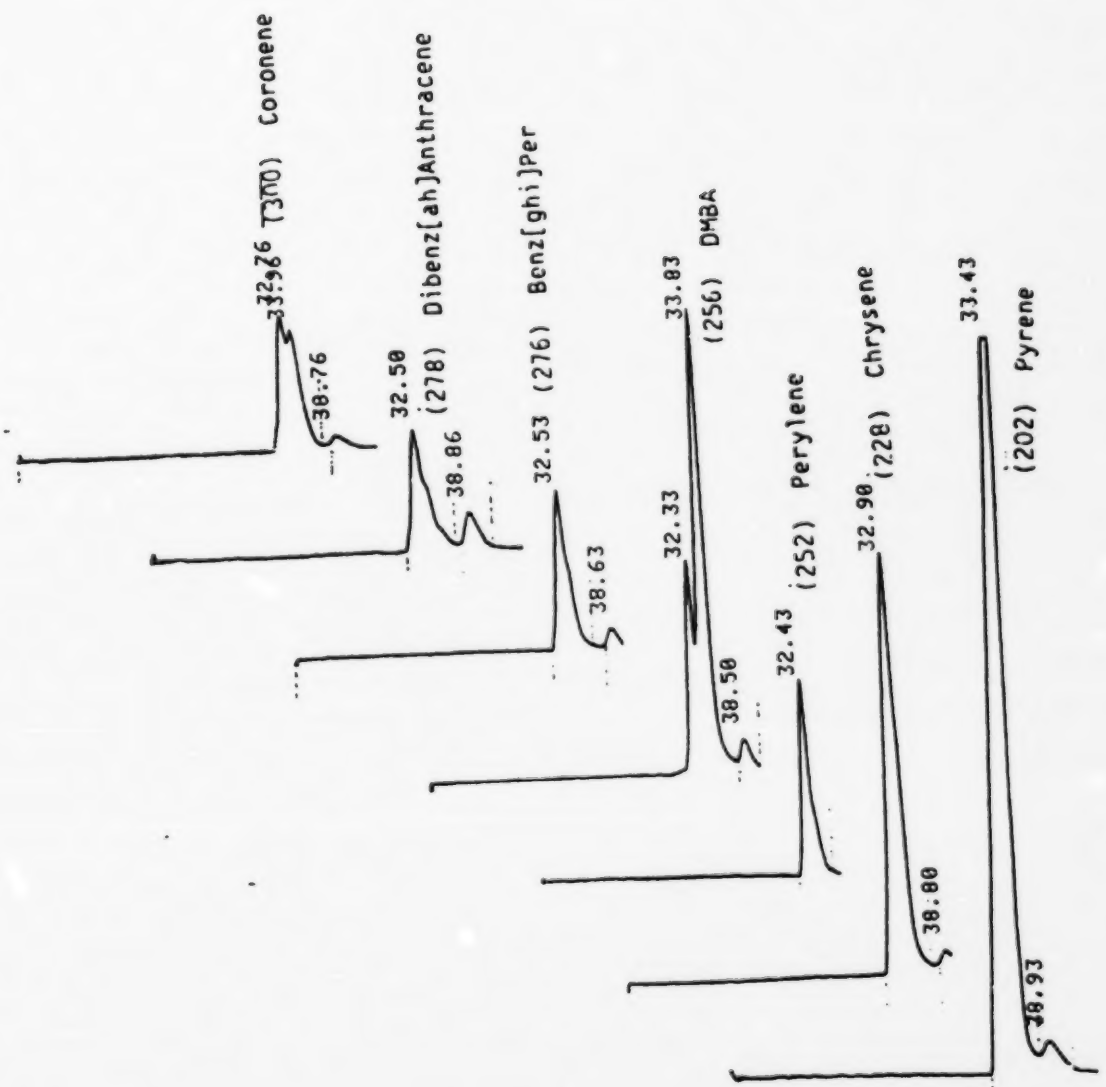


Figure 37D: SEC Profiles of Model Compounds - Saturates
Conditions: 2 x zorbax PSM 60-S/O-xylene/35°C/
0.3 ml/min (Retention Time Data in Table 13)